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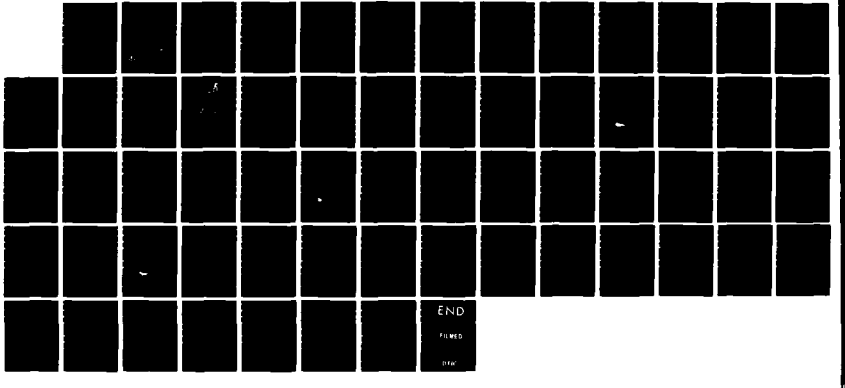

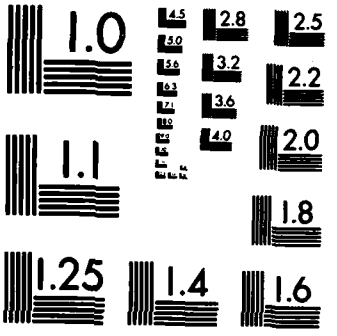

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HIGH RATE Li/$SOC1_2$ CELLS
II. EFFECT OF CATALYST ON CELL PERFORMANCE

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RESEARCH AND TECHNOLOGY DEPARTMENT

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Co-TAA catalyst improved the performance and safety of C-size $Li/SOCl_2$ cells. The catalyst was most effective at high rate or low temperature operation. The presence of water increased the risk of hazards at high rates of discharge. The generation of gases such as COS, CS_2, HCl, etc. was dependent on the internal temperature. Originator supplied keywords - Include?

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FOREWORD

The $Li/SOCl_2$ battery system has received considerable interest for a number of high rate, high energy Naval applications. However, high rate applications increase the risk of safety hazards to Naval personnel.

To enhance rate capability, a Co-TAA catalyst has been added to $Li/SOCl_2$ cells. This report examines the effects of this catalyst on the performance, safety, and chemistry of various specially instrumented $Li/SOCl_2$ cells discharged and forced overdischarged at -12°C and ambient temperatures.

Funding for this work was provided by the NAVSEA High Energy Batteries for Weapons Block Program.

Approved by:

J. R. Dixon

JACK R. DIXON, Head
Materials Division

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CHAPTER 1

INTRODUCTION

As part of the ongoing High Energy Batteries for Weapons Programs at NSWC, various cell parameters were investigated to examine their effect on the performance, safety, and chemistry of $Li/SOCl_2$ cells. This report summarizes the influence of cobalt dibenzo-tetraazaannulene (Co-TAA) catalysis on the discharge and overdischarge chemistry and performance of spirally wound commercial C-size cells.

This investigation was undertaken because a recent paper claimed that TAA complexes dramatically enhanced cell performance and altered the electrochemical mechanism so that no SO_2 gas pressure was generated.[1] An SO_2 free $SOCl_2$ system would offer a significant improvement in safety.

Since this study began, a second report by these authors proposed a different SO_2 free cell discharge mechanism than the one they first proposed.[2] Although this investigation did not focus on elucidating the reaction mechanism, our data indicate the catalyst does not alter the $Li/SOCl_2$ cell chemistry to produce an SO_2 free cell.

CHAPTER 2

EXPERIMENTAL

The C-size cells were prepared by Hellesens Battery Engineering, Hyde Park, Ma., according to standard manufacturing procedures. The cell specifications and testing procedures have been described in the first report.[3] Cells are classified as Dry and Wet cells. The latter contained 500 ppm added H_2O.

Cathodes were prepared from Shawinigan acetylene black. In addition to the regular cathodes, cathodes containing 5 weight percent of a tetraazaannulene complex of cobalt (Co-TAA) as a catalyst additive were used. The catalyzed cathodes were prepared by mixing the carbon with the catalyst and the mixture was heat treated at 500°C under inert gas. After cooling, this mixture was made into a paste with water, isopropanol and Teflon binder, followed by drying below 100°C. The mixture was cured by heating to ~275°C under inert gas. At no time was the catalyst heated above 100°C in air. The preparation and application techniques have previously been described in reports[2,4] and a recent patent.[5]

CHAPTER 3

RESULTS

The data obtained with the catalyzed Li/$SOCl_2$ cells are described below. This data can be compared with the uncatalyzed cell data described in the first report.[3]

CATALYZED LITHIUM-LIMITED CELLS

Dry Cells at 20°C

Catalyzed Li-limited dry cells, labelled C-A-D were overdischarged at 0.2, 2.0, 3.0, and 4.0A at 20°C. None of the cells vented. Cell data are summarized in Table 1. Representative performance data are illustrated in Figures 1 through 4.

Cells C-A-D-1 and C-A-D-2 were manually vented and each cell was analyzed. The IR spectra of the gases released showed only SO_2 and $SOCl_2$. GC analyses showed that CO_2 and a trace of COS was present in each cell discharged above the 0.2A rate.

The IR spectra of the salts collected from these cells were identical to the spectrum of salts previously collected from uncatalyzed Li-limited cells. The IR spectrum of salts extracted from cell C-A-D-2 is shown in Figure 5. IR analyses of the cathodes showed only weak absorptions from $LiAlCl_4$. Chemical spot tests for $S_2O_4^{2-}$, $S_2O_3^{2-}$, S^{2-}, SO_3^{2-}, and SO_4^{2-} were negative.

Dry Cells at -12°C

Table 2 summarizes the data from catalyzed Li-limited cells discharged at -12°C. At this low temperature the capacity is the same as found at room temperature but the mid-discharge voltage is lower. Discharge data are illustrated in Figures 6 and 7. The anode potential of cell C-A-D-12 displays a rise-fall behavior characteristic of the anodic polarization phenomenon previously observed in several cathode limited cells, with the distinction that the lithium anode potential rises presumably from lithium depletion.

TABLE 1. PERFORMANCE OF CATALYZED LITHIUM-LIMITED DRY CELLS AT 20°C

Cell Number	Discharge Current (A)	Current Density (mA/cm^2)	Capacity to 0.0V (A-hr)	Maximum Temp. (°C)	Maximum Pressure (psig)	Mid-discharge Voltage (V)
C-A-D-1	0.2	0.8	3.24	31	21	3.52
C-A-D-2	2.0	8.0	2.96	67	55	3.40
C-A-D-3	2.0	8.0	2.92	73	52	3.40
C-A-D-4	2.0	8.0	2.92	67	60	3.40
C-A-D-5	2.0	8.0	2.92	60	70	3.40
C-A-D-6	2.0	8.0	3.20	60	50	3.40
C-A-D-7	3.0	11.9	2.92	74	37	3.19
C-A-D-8	4.0	15.8	3.06	117	130[1]	3.11
C-A-D-9	4.0	15.8	3.24	-	100	3.12

[1]Cell leaked through transducer connection to cell.

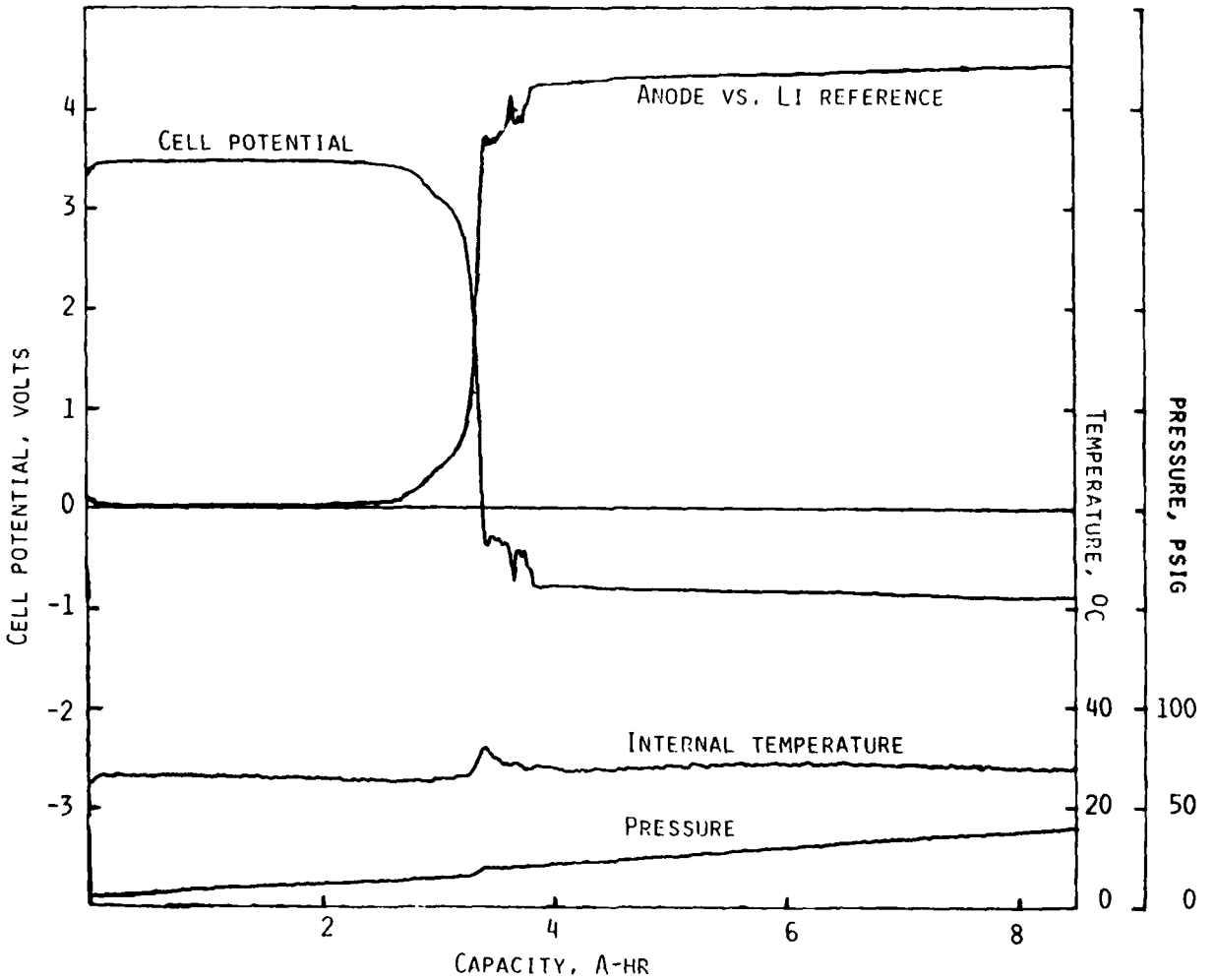


FIGURE 1. DISCHARGE DATA FOR CELL C-A-D-1 AT 0.2A AND 20°C

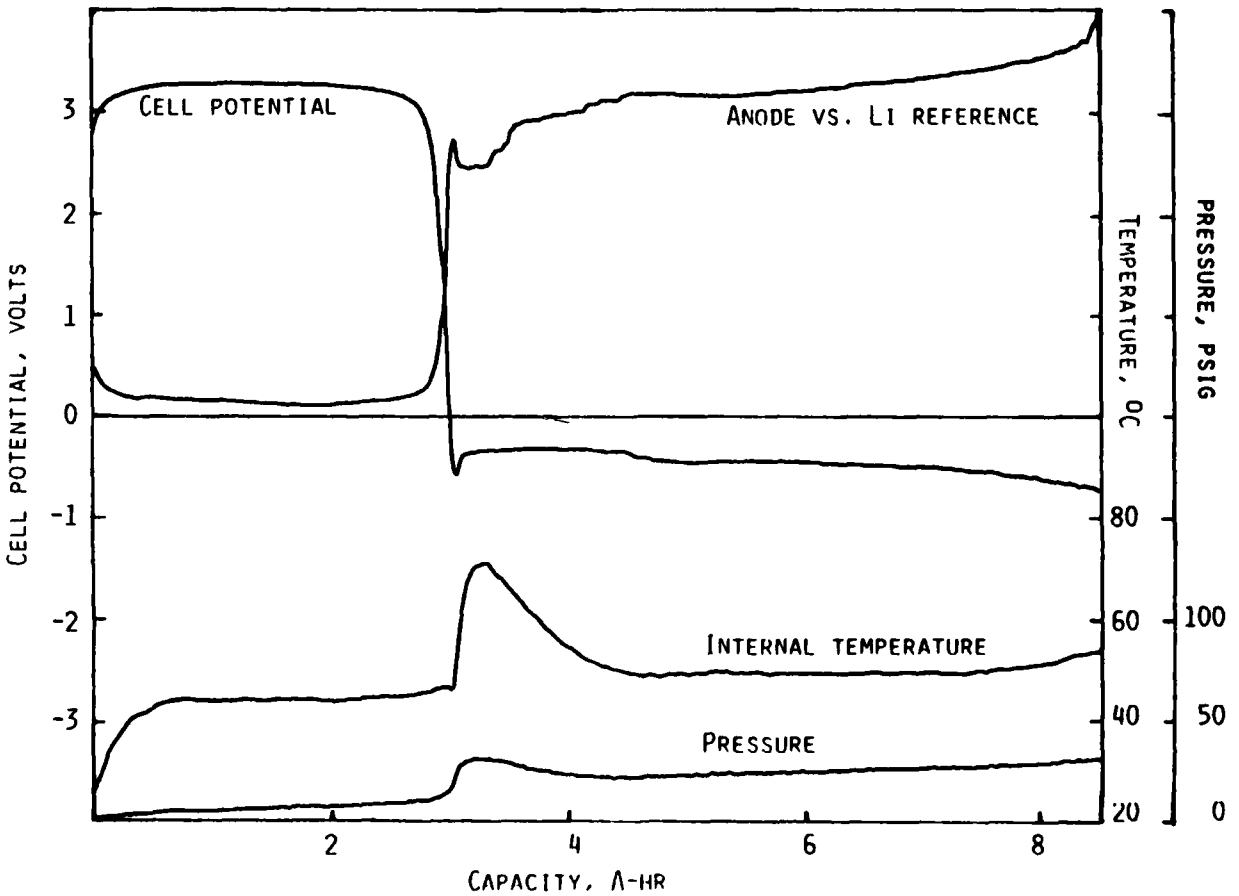


FIGURE 2. DISCHARGE DATA FOR CELL C-A-D-2 AT 2.0A AND 20°C

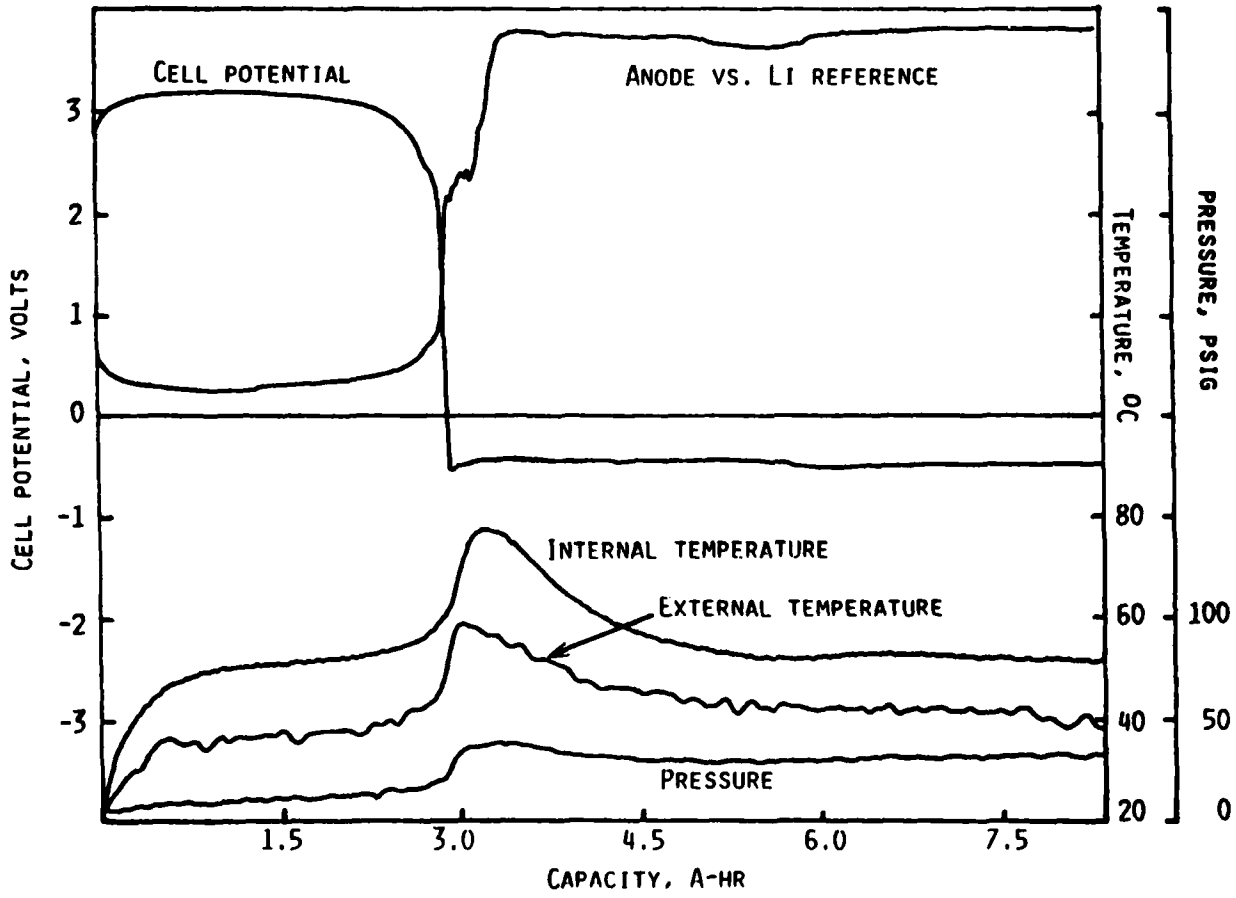


FIGURE 3. DISCHARGE DATA FOR CELL C-A-D-7 AT 3.0A AND 20°C

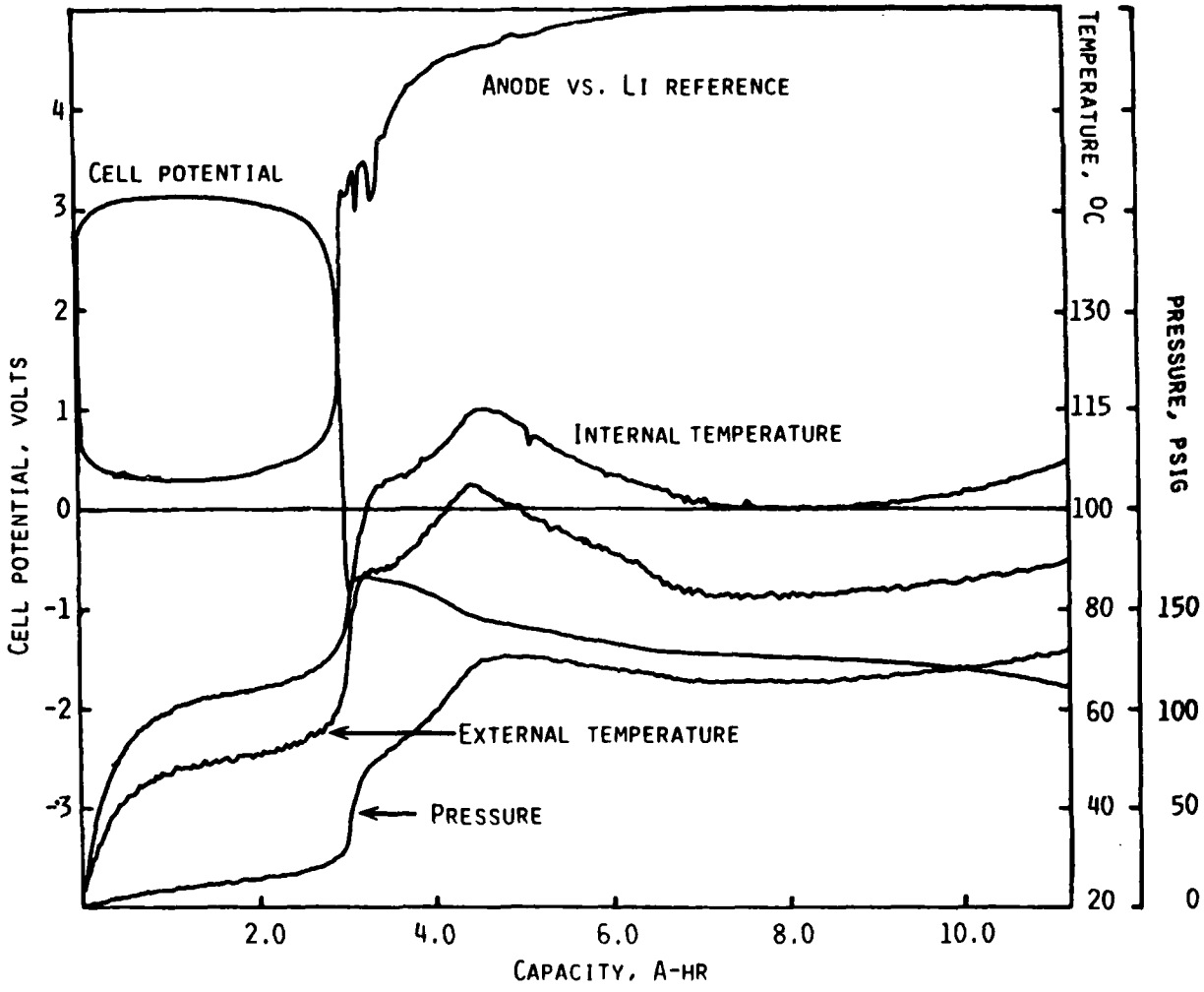


FIGURE 4. DISCHARGE DATA FOR CELL C-A-D-8 AT 4.0A AND 20°C

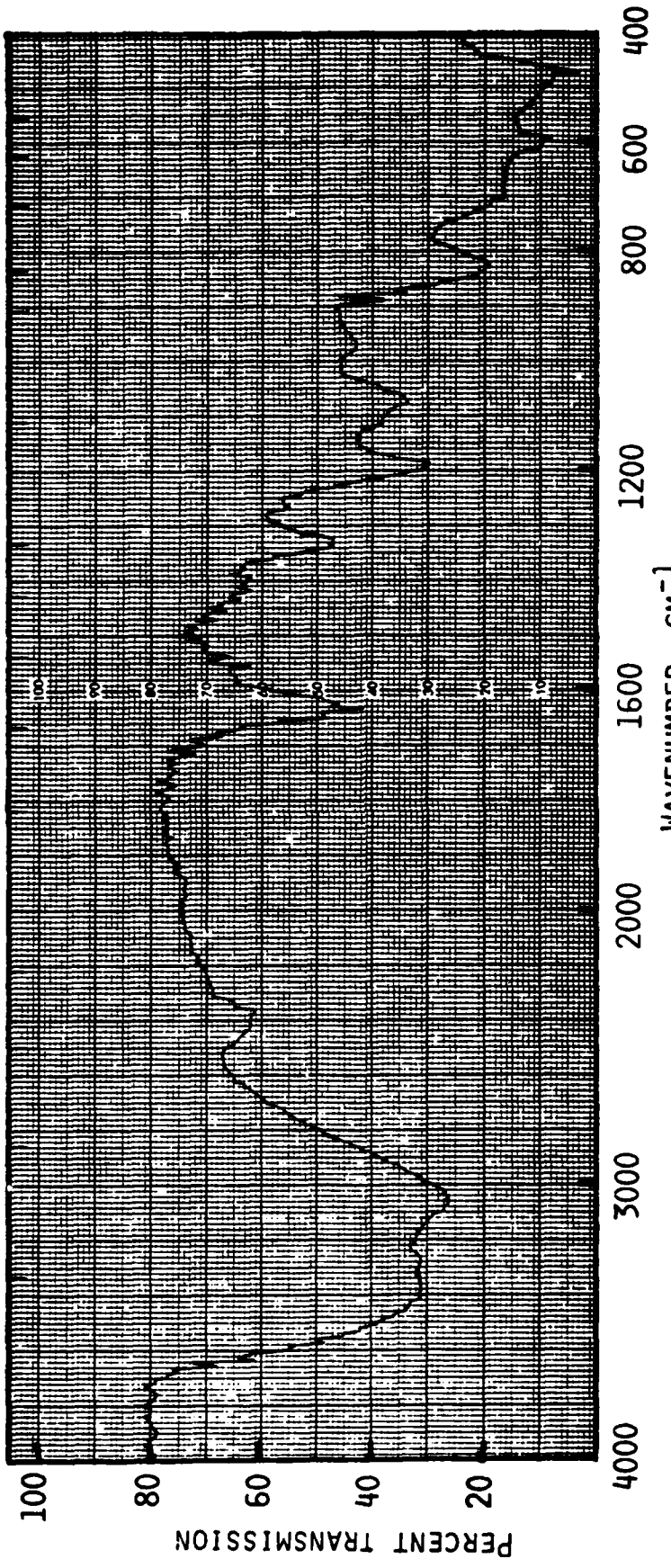


FIGURE 5. IR SPECTRUM OF SALTS FROM CELL C-A-D-2

TABLE 2. PERFORMANCE OF CATALYZED LITHIUM-LIMITED DRY CELLS AT -12°C

Cell Number	Discharge Current (A)	Current Density (mA/cm^2)	Capacity to 0.0V (A-hr)	Maximum Temp. (°C)	Maximum** Pressure (psig)	Mid-discharge Voltage (V)
C-A-D-10	0.2	0.8	3.12	-4	0	3.35
C-A-D-11	2.0	8.0	2.46	43	0	3.05
C-A-D-12	2.0	8.0	3.07	43	2.5	3.05
C-A-D-13*	2.0	8.0	3.18	Off-scale	40	3.05

* Cell was initially charged for 2.58 A-hr.
**The pressure transducer response at -12°C was poor and its measured value may be low.

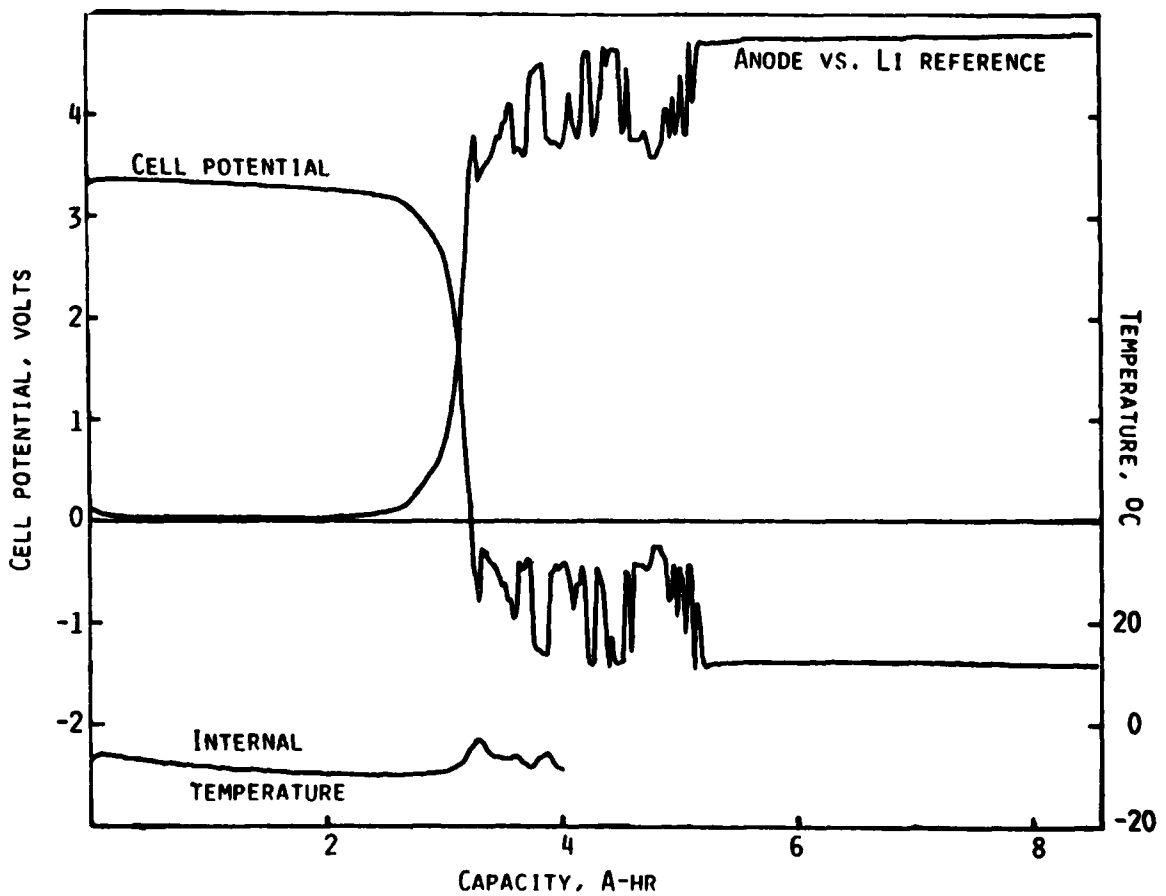


FIGURE 6. DISCHARGE DATA FOR CELL C-A-D-10 AT 0.2A AND –12°C

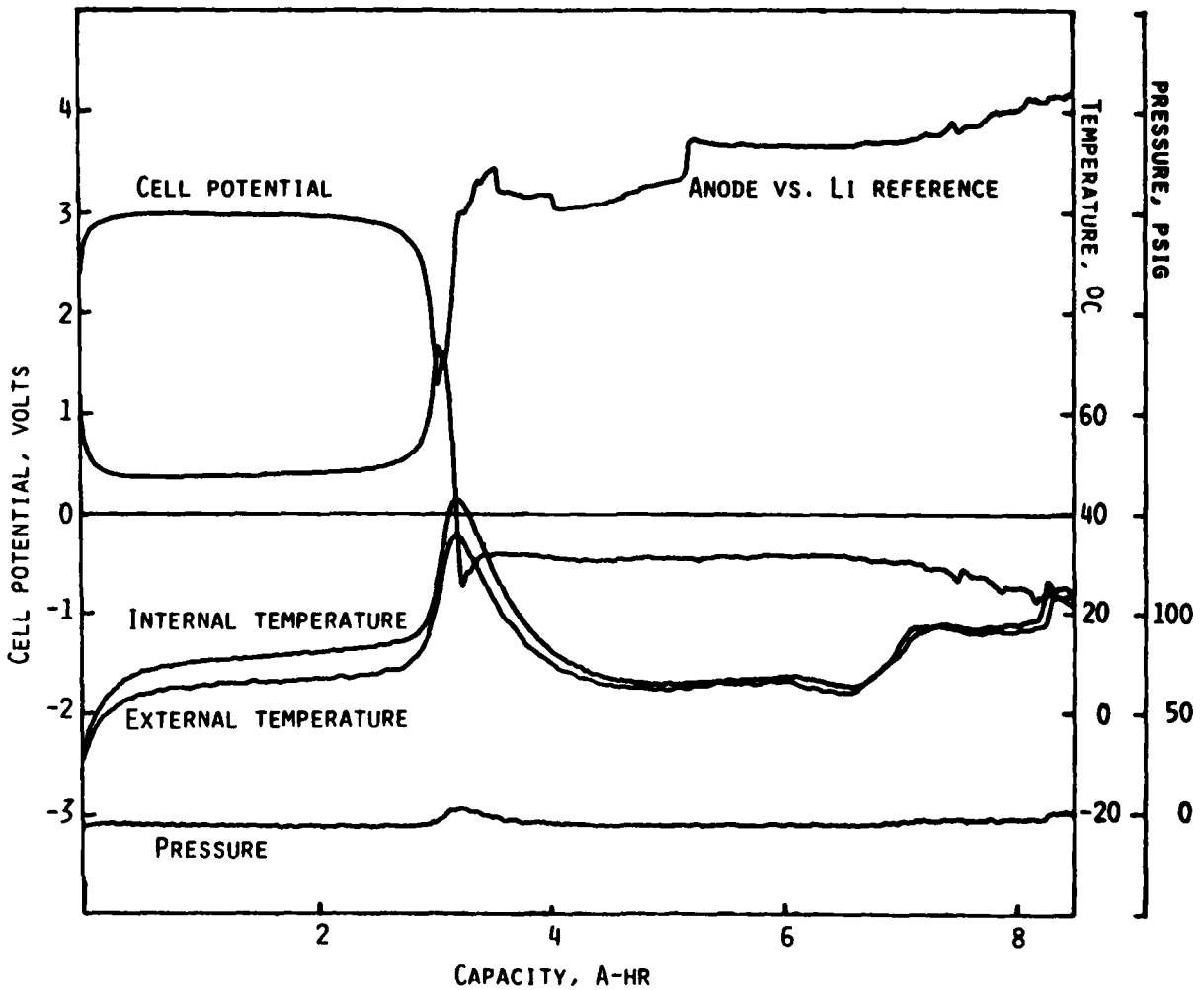


FIGURE 7. DISCHARGE DATA FOR CELL C-A-D-12 AT 2.0A AND −12°C

Chemical analyses of the gases, extracted solids and carbon cathode were similar to the cells at 20°C with one exception - no COS was detected.

Wet Cells at 20°C

The performance of catalyzed Li-limited wet cells at 20°C are summarized in Table 3. Only the cells overdischarged at 4.0A or higher currents vented. Cell C-A-W-19 vented through the bottom of the cell. The pressure was not recorded on the pressure transducer. The discharge curve for cell C-A-W-21 discharged at 5.0A is shown in Figure 8.

Chemical analyses of overdischarged cells yielded the same results as found in the dry cells at the 0.2 and 2.0A rates. No COS was found at the 0.2A rate. A small amount appears at the 4.0A rate. At the 4.0A rate, the COS is observed as a weak doublet at 2020 cm^{-1}. At the 5.0A rate, the COS band is appreciable (Figure 9).

Wet Cells at -12°C

Cell discharge performance data at -12°C are summarized in Table 4. The discharge data at the 4.0A rate is illustrated in Figure 10. This cell did not vent. IR analysis of the gases released after manual venting showed only SO_2 and $SOCl_2$. No HCl or COS absorptions were present.

CATALYZED CATHODE-LIMITED CELLS

Dry Cells at 20°C

The performance data for catalyzed cathode-limited dry cells, labelled C-C-D, are shown in Table 5. Performance behavior for representative cells are illustrated in Figures 11 through 14.

Cell C-C-D-2 was manually vented after forced overdischarge and chemically analyzed. IR gas analysis again showed SO_2 and $SOCl_2$. GC analysis revealed CO_2 and COS. COS was present in higher quantity than in similarly discharged Li-limited cells. IR analysis of the cathode revealed a new peak at 1015 cm^{-1} which was not previously observed.

The high rate discharge data obtained at the 3.0A rate (Table 5) indicated that the venting threshold was not reproducible. The pressure in the unvented cells exceeded the pressure in the cell that vented. The pressure curve for cell C-C-D-4, shown in Figure 13, indicates the venting occurred when the internal temperature peaked at 146°C. The temperature drops and then increases rapidly. It may be that another reaction occurs after venting. Cell C-C-D-8 which vented on overdischarge at a 4.0A rate (Figure 14) exhibited no such behavior. After the cell reached 345 psi, the pressure decreases slowly while the temperature curve shows no increase after venting.

TABLE 3. PERFORMANCE OF CATALYZED LITHIUM-LIMITED WET CELLS AT 20°C

Cell Number	Discharge Current (A)	Current Density (mA/cm^2)	Capacity to 0.0V (A-hr)	Maximum Temp. (°C)	Maximum Pressure (psig)	Mid-discharge Voltage (V)
C-A-W-14	0.2	0.8	3.32	32	50	3.52
C-A-W-15	0.2	8.0	3.24	63	58	3.40
C-A-W-16	2.0	8.0	3.06	63	55	3.31
C-A-W-17	2.0	8.0	3.18	62	47	3.30
C-A-W-18	2.0	8.0	3.10	70	46	3.30
C-A-W-19*	4.0	15.8	3.02	145[1]	-	3.15
C-A-W-20*	4.0	15.8	2.88	99[2]	218	3.10
C-A-W-21*	5.0	20.8	2.90	Off-scale[3]	188	3.08

*Cell vented
[1]Temperature reached after 7 hours forced overdischarge.
[2]External temperature (cell leaked).
[3]Temperature went off-scale after cell vented.

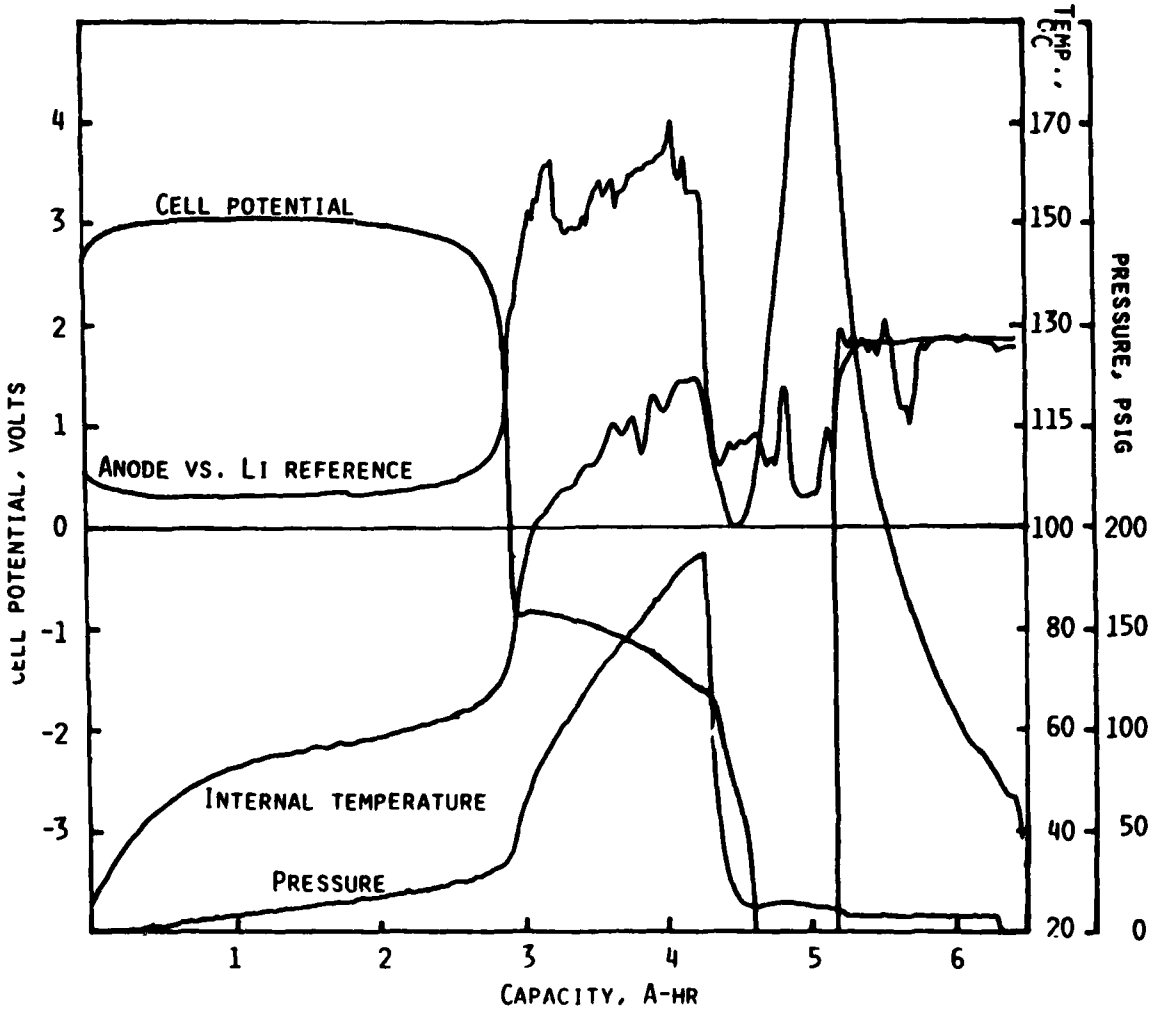


FIGURE 8. DISCHARGE DATA FOR CELL C-A-W-21 AT 5.0A AND 20°C

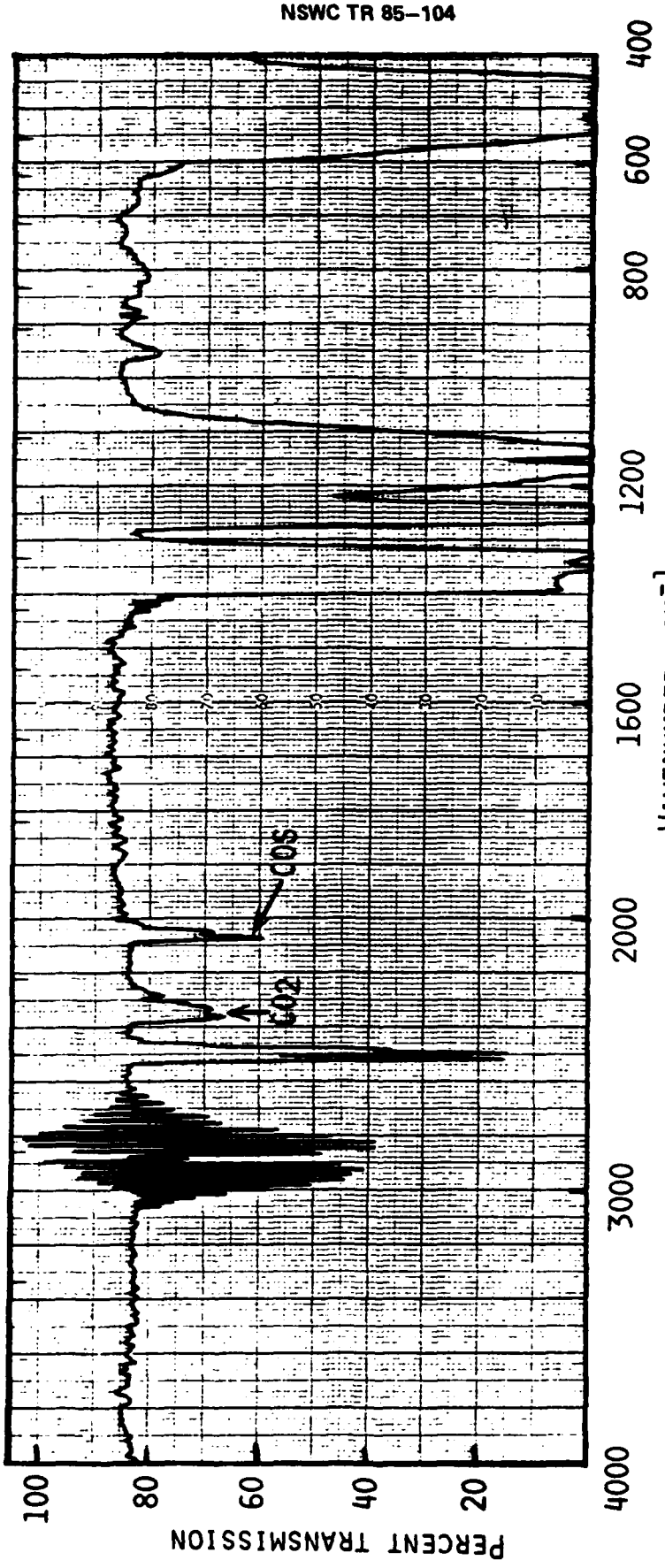


FIGURE 9. IR SPECTRUM OF GASES RELEASED FROM CELL C-A-W-21

TABLE 4. PERFORMANCE OF CATALYZED LITHIUM-LIMITED WET CELLS AT -12°C

Cell Number	Discharge Current (A)	Current Density (mA/cm^2)	Capacity to 0.0V (A-hr)	Maximum Temp. (°C)	Maximum* Pressure (psig)	Mid-discharge Voltage (V)
C-A-W-22	0.2	0.8	3.12	10	-	3.37
C-A-W-23	2.0	8.0	3.35	52	8	2.98
C-A-W-24	2.0	8.0	2.96	41	12	2.98
C-A-W-25	2.0	8.0	3.19	42	10	3.01
C-A-W-26	4.0	15.8	3.12	54	35	2.83

*The pressure transducer response at -12°C was poor and the pressure value may be low.

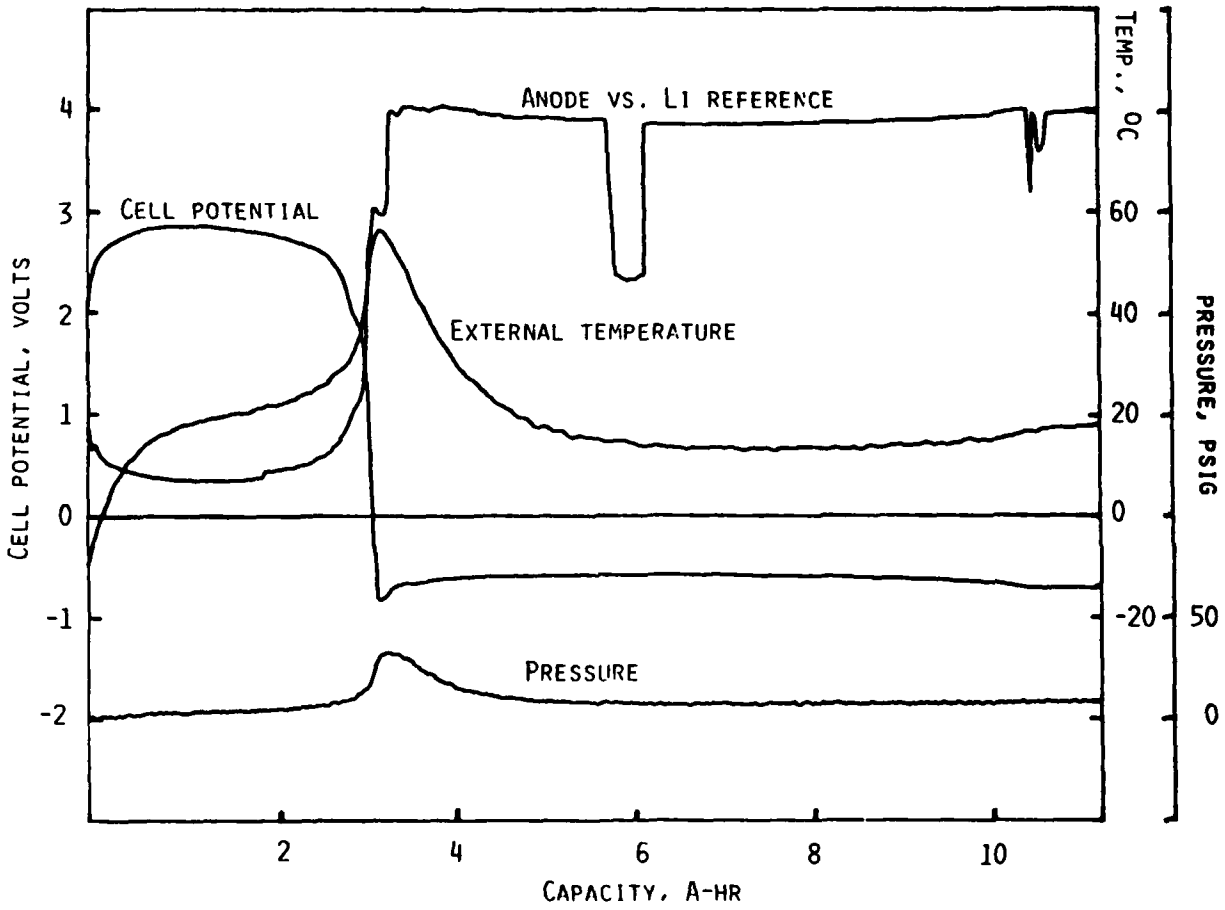


FIGURE 10. DISCHARGE DATA FOR CELL C-A-W-26 AT 4.0A AND −12°C

TABLE 5. PERFORMANCE OF CATALYZED CATHODE-LIMITED DRY CELLS AT 20°C

Cell Number	Discharge Current (A)	Current Density (mA/cm^2)	Capacity to 0.0V (A-hr)	Maximum Temp. (°C)	Maximum Pressure (psig)	Mid-discharge Voltage (V)
C-C-D-1	0.2	1.0	5.28	37	20	3.52
C-C-D-2	2.0	10.0	4.39	107	68	3.30
C-C-D-3	2.0	10.0	4.24	96	80	3.28
C-C-D-4*	3.0	15.0	3.87	>190	205	3.20
C-C-D-5	3.0	15.0	4.00	116	255	3.20
C-C-D-6	3.0	15.0	3.94	143	247	3.18
C-C-D-7	3.0	15.0	3.98	154	240	3.20
C-C-D-8*	4.0	20.0	3.53	117**	345	3.15
C-C-D-9	4.0	20.0	3.38	148	270	3.10

* Cells vented.
**Internal thermocouple not positioned in middle of cell.

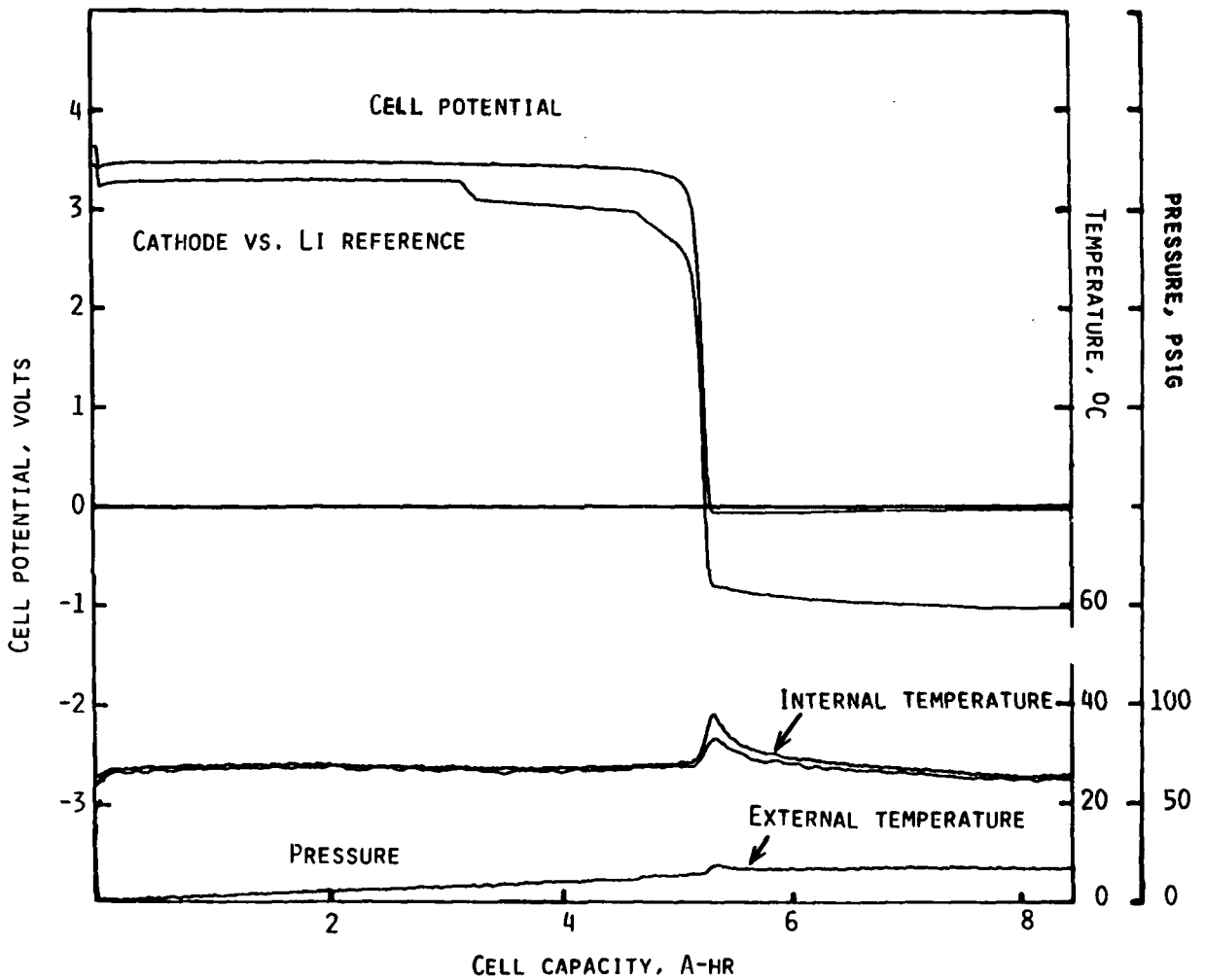


FIGURE 11. DISCHARGE DATA FOR CELL C-C-D-1 AT 0.2A AND 20°C

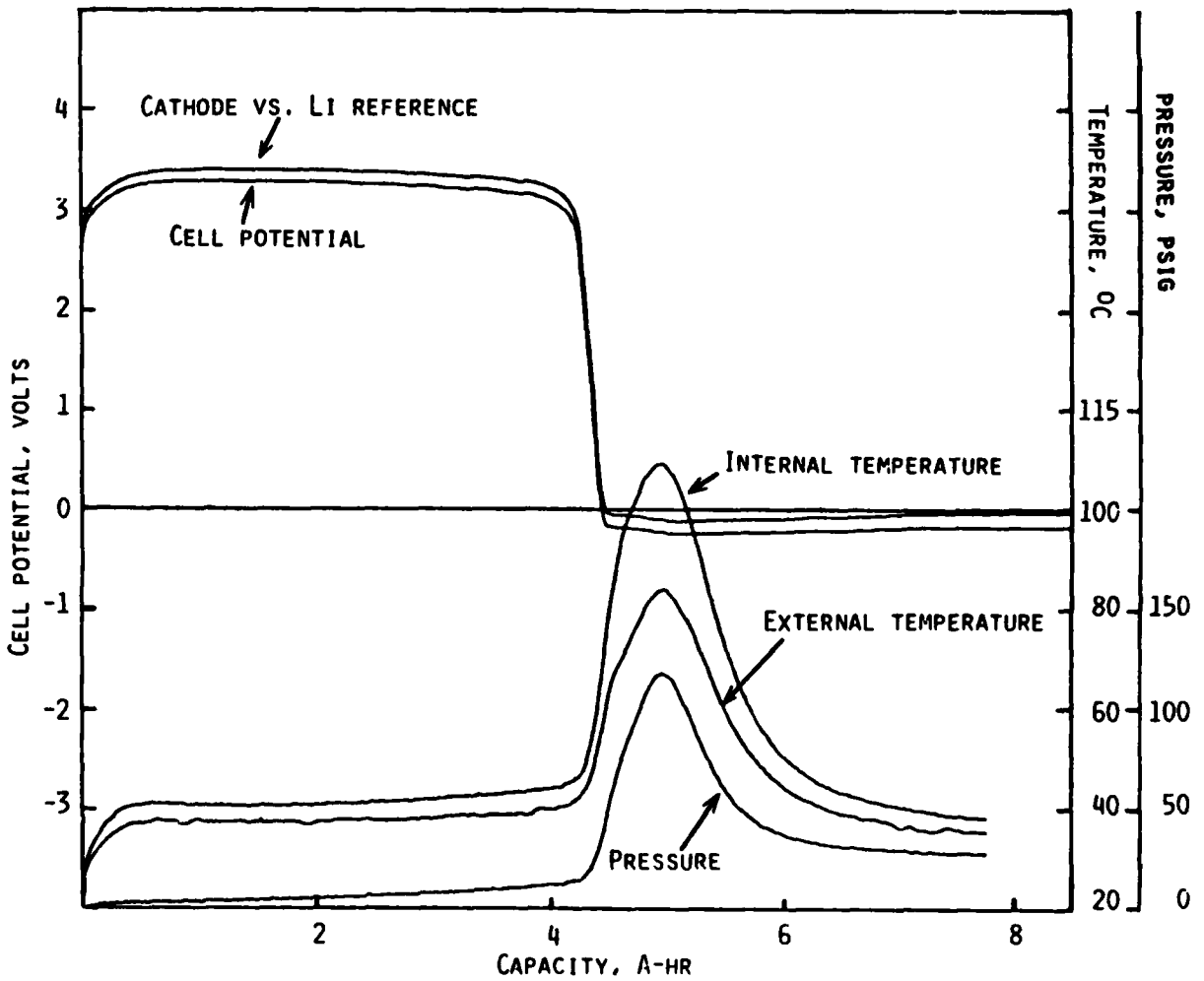


FIGURE 12. DISCHARGE DATA FOR CELL C-C-D-2 AT 2.0A AND 20°C

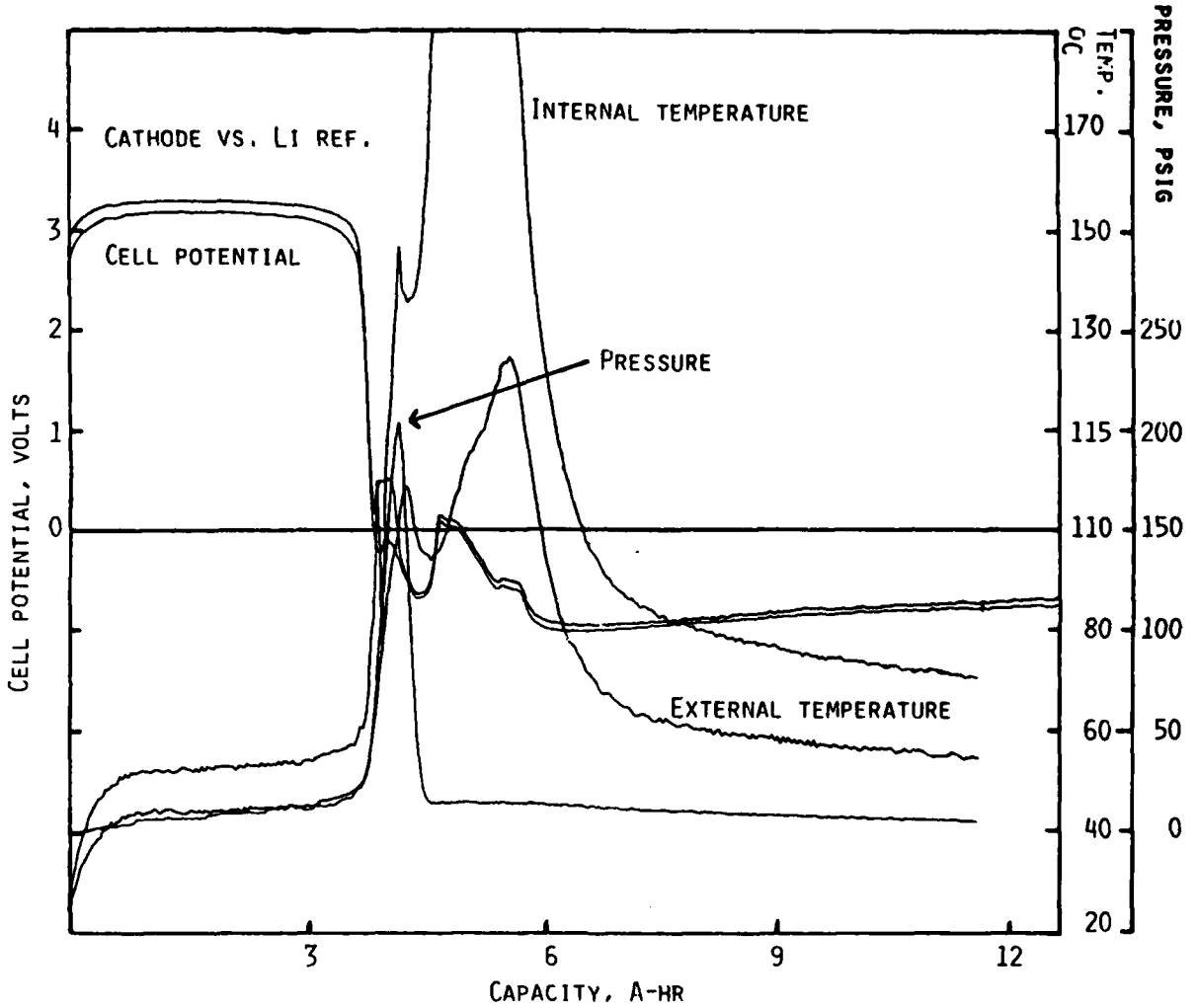


FIGURE 13. DISCHARGE DATA FOR CELL C-C-D-4 AT 3.0A AND 20°C

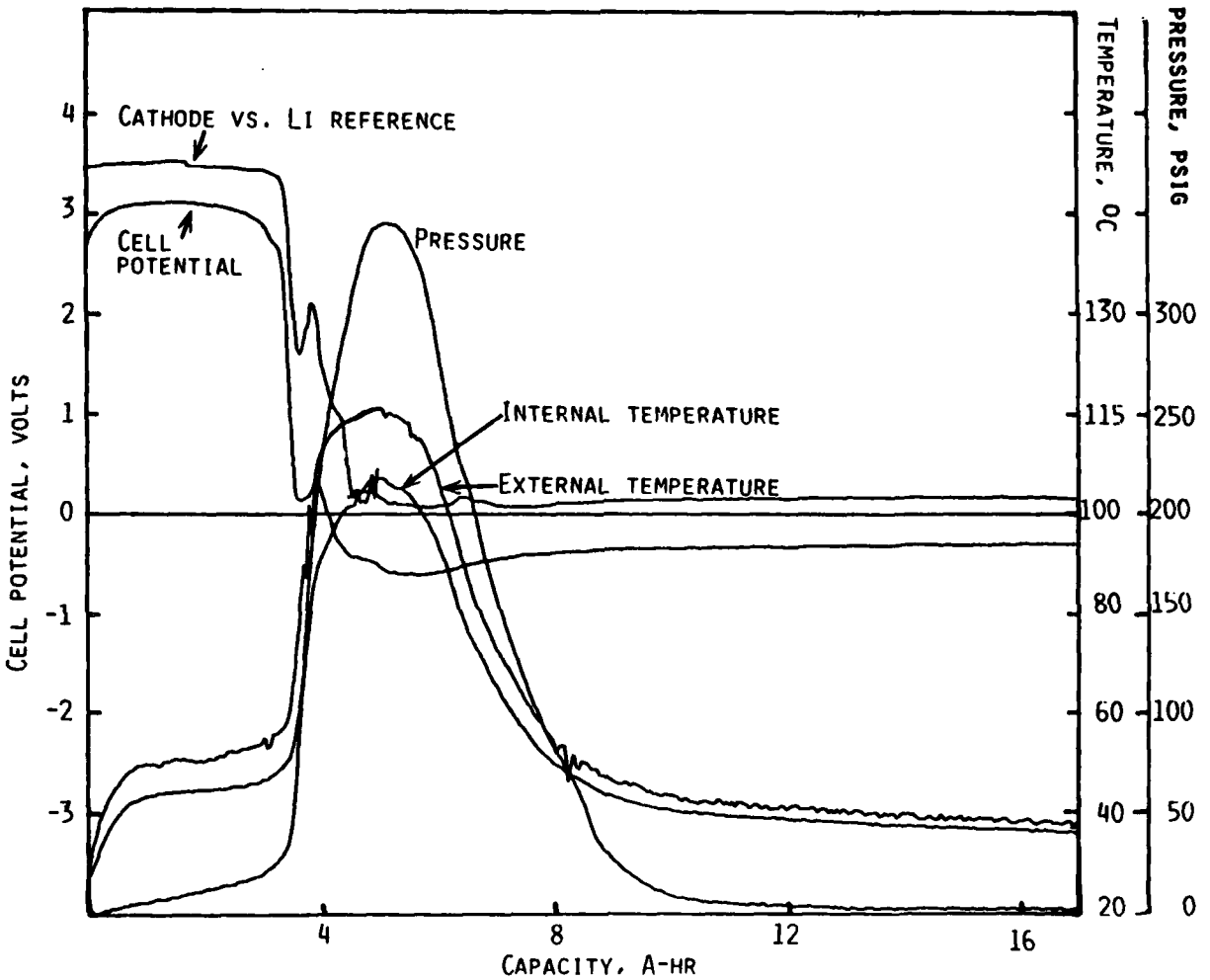


FIGURE 14. DISCHARGE DATA FOR CELL C-C-D-8 AT 4.0A AND 20°C

Gas analysis of cells C-C-D-4 (tested at 3.0A) and C-C-D-8 (tested at 4.0A) also show differences. A large amount of HCl was found in cell C-C-D-4. Cell C-C-D-8 which exhibited no second reaction after venting contained no HCl but a substantial amount of COS was present with absorptions near 2065 cm^{-1}. The results can be compared in Figures 15 and 16.

Gas analysis of cell C-C-D-5 which was manually vented showed no HCl to be present.

Dry Cells at -12°C

The results of cells discharged at -12°C are summarized in Table 6. Discharge data obtained the 2.0 and 3.0A rates are shown in Figures 17 and 18, respectively.

Chemical analyses were performed on cells discharged at the 0.2, 2.0, and 3.0A rates. The analyses gave the same results as found in the cells discharged at 20°C. The unvented cells showed SO_2 and $SOCl_2$ in the gas phase. The IR band at 1015 cm^{-1} was again present and is shown in Figure 19.

Wet Cells at 20°C

The discharge data for the wet cells, labelled C-C-W, are summarized in Table 7. Typical performance data obtained at each rate is illustrated in Figures 20 through 23.

IR analyses of the unvented cells discharged at 0.2 and 2.0A rates showed only SO_2 and $SOCl_2$ gases present. Cell C-C-W-21, which displayed two temperature peaks after cell venting, also exhibited HCl in the IR spectrum. These results are similar to the data observed at 20°C for dry cells.

Cell C-C-W-24 displayed the most violent behavior so far (see Figure 23). The discharge curves are very similar to cell C-C-D-4. The internal temperature goes off-scale, but the external temperature shows a drop in temperature after venting and then it too goes off scale. The gas phase IR spectrum for cell C-C-W-24 is shown in Figure 24. In addition to the SO_2 and $SOCl_2$, there are very strong absorptions for HCl, COS, CO_2 and a doublet at 1530 and 1545 cm^{-1} belonging to CS_2.

Wet Cells at -12°C

The data for the catalyzed cathode limited wet cells at -12°C, labelled C-C-W, are shown in Table 8. Discharge data at the 2.0 and 3.0A rates are illustrated by Figures 25 and 26, respectively.

IR gas analysis of the unvented cells showed only SO_2 and $SOCl_2$ present. The wet cells discharged at 4.0A vented. Vapor phase IR analysis showed the same products as those found in vented cells discussed above.

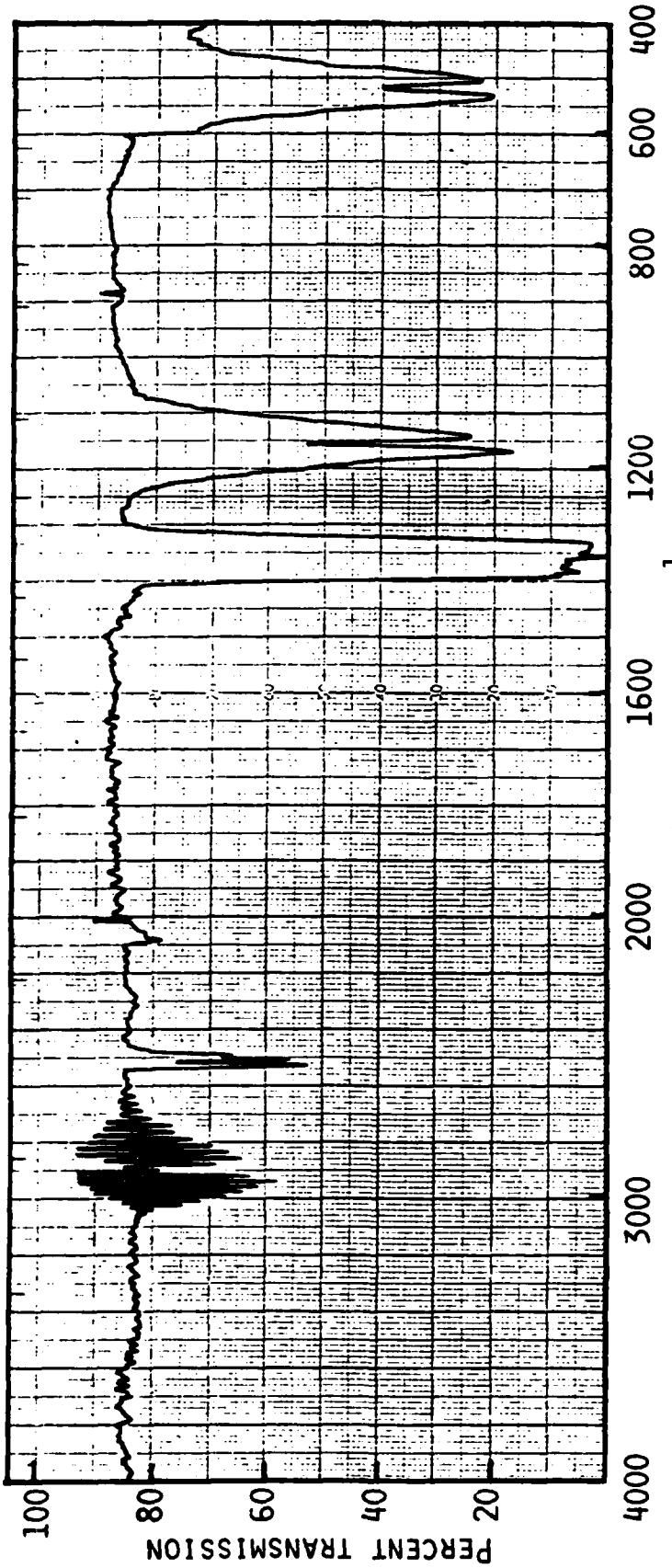


FIGURE 15. IR SPECTRUM OF GASES RELEASED DURING THE VENTING OF CELL C-C-D-4

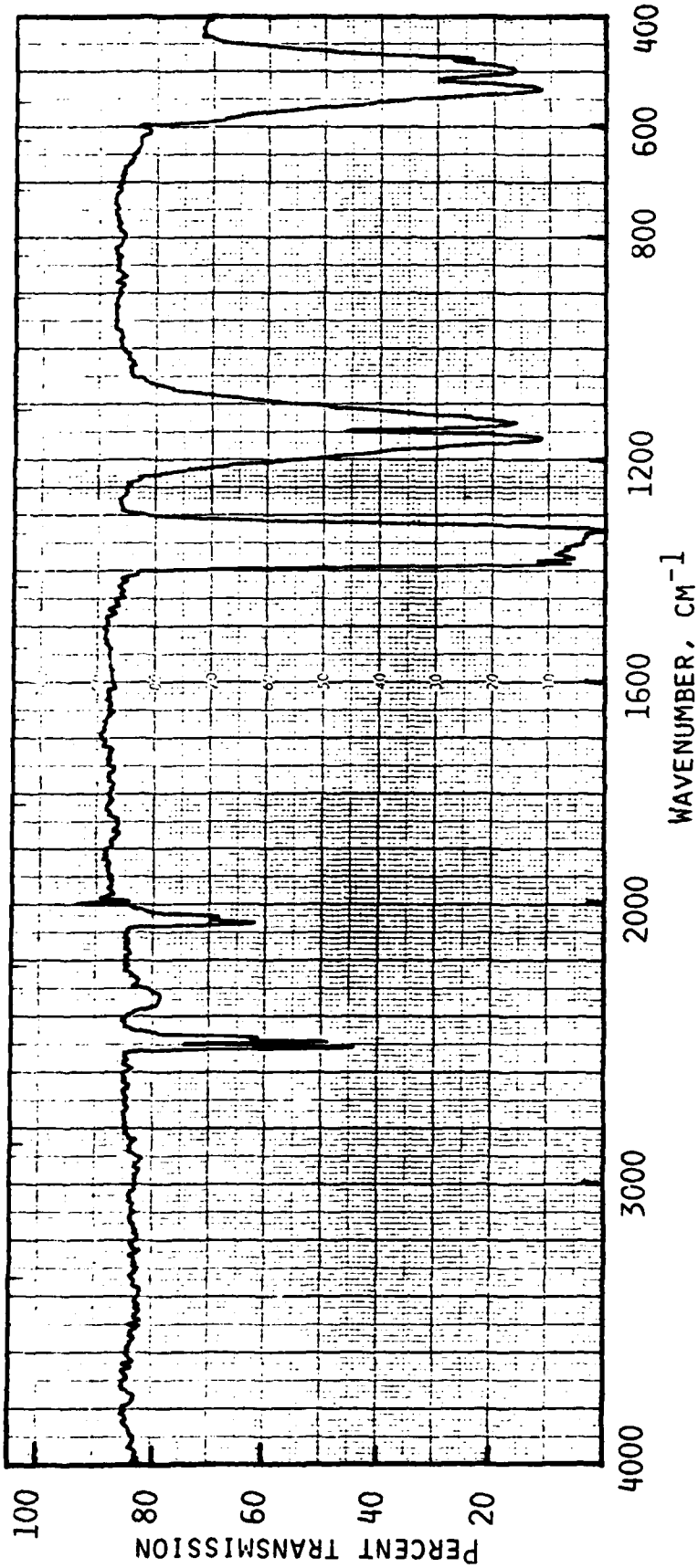


FIGURE 16. IR SPECTRUM OF GASES RELEASED FROM CELL C-C-B-8 AFTER VENTING

TABLE 6. PERFORMANCE OF CATALYZED CATHODE-LIMITED DRY CELLS AT -12°C

Cell Number	Discharge Current (A)	Current Density (mA/cm^2)	Capacity to 0.0V (A-hr)	Maximum Temp. (°C)	Maximum Pressure (psig)	Mid-discharge Voltage (V)
C-C-D-10	0.2	1.0	4.72	4	0	3.18
C-C-D-11	2.0	10.0	3.61	74	32	2.85
C-C-D-12	2.0	10.0	3.42	64	20	2.70
C-C-D-13	3.0	15.0	3.46	-	102	2.85
C-C-D-14	3.0	15.0	3.44	96*	75	2.92
C-C-D-15	3.0	15.0	3.28	131	130	2.90
C-C-D-16	4.0	20.0	2.83	144	-	2.52
C-C-D-17	4.0	20.0	2.64	97*	145	2.40

*External cell temperature.

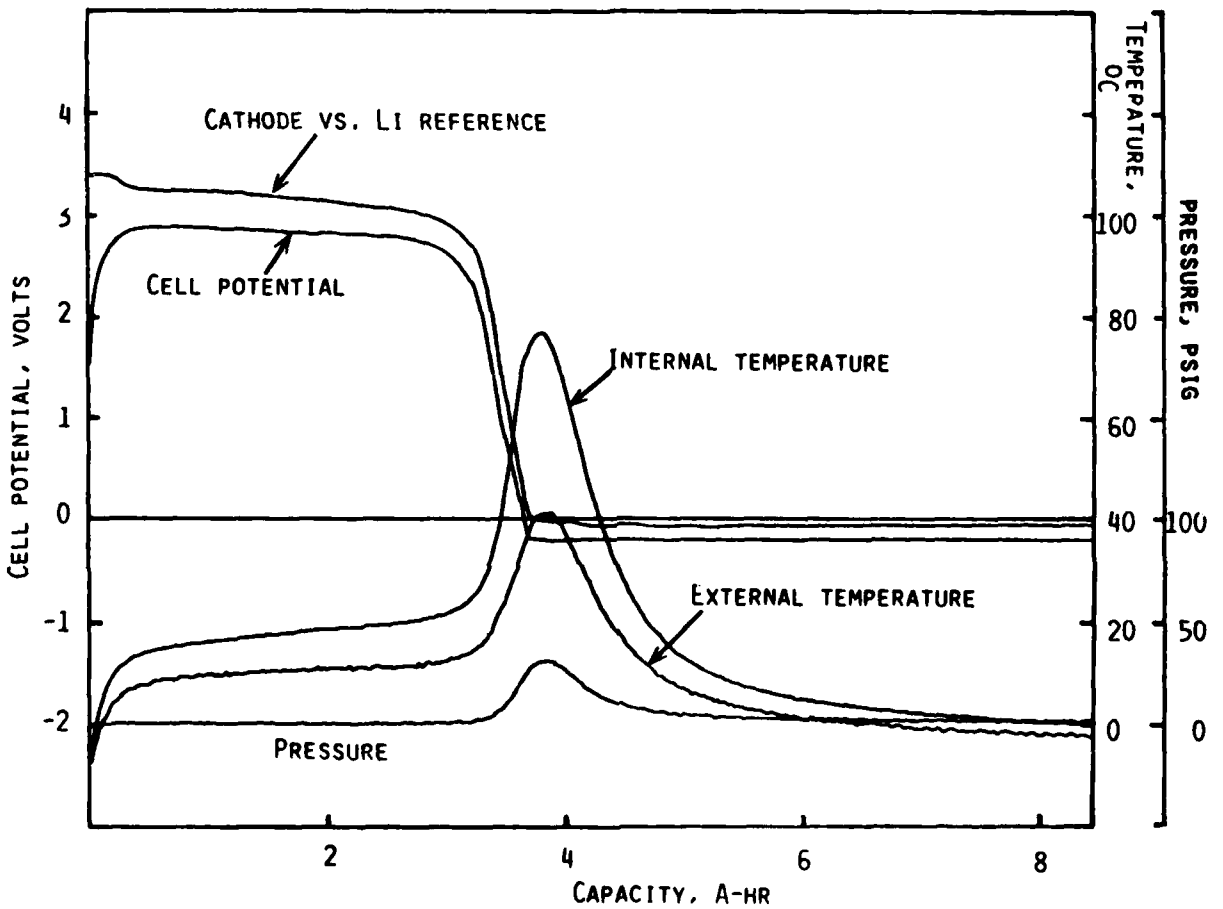


FIGURE 17. DISCHARGE DATA FOR CELL C-C-D-11 AT 2.0A AND −12°C

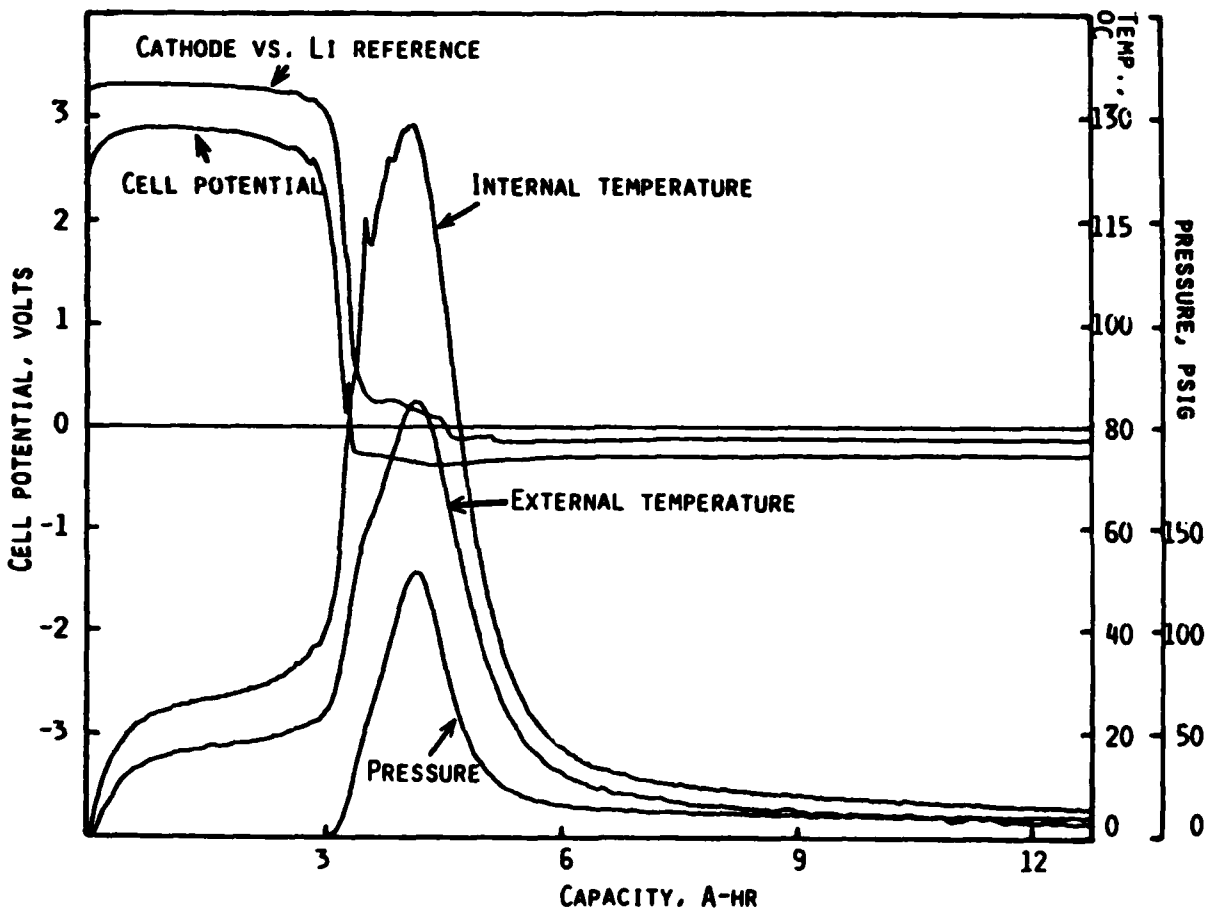


FIGURE 18. DISCHARGE DATA FOR CELL C-C-D-15 AT 3.0A AND −12°C

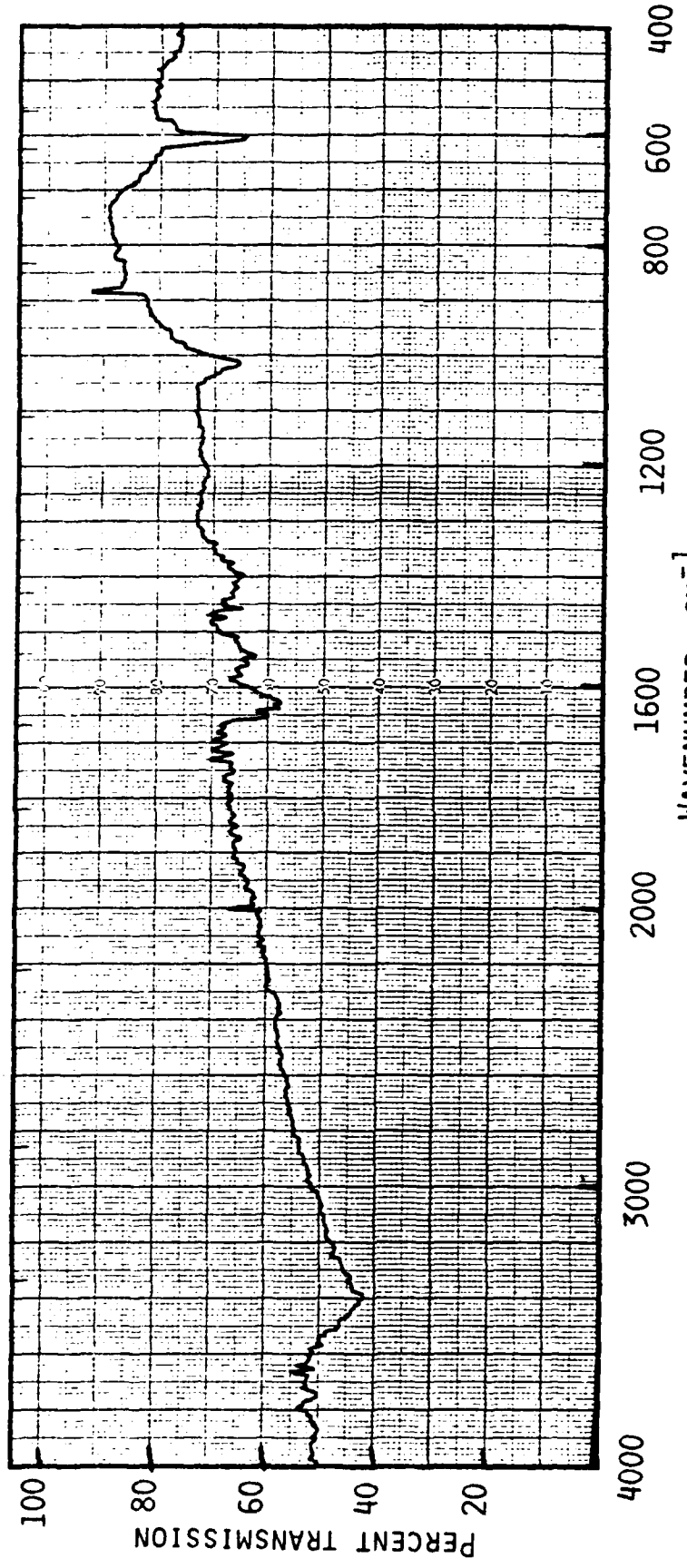


FIGURE 19. IR SPECTRUM OF THE CATHODE OF CELL C-C-D-11

TABLE 7. PERFORMANCE OF CATALYZED CATHODE-LIMITED WET CELLS AT 20°C

Cell Number	Discharge Current (A)	Current Density (mA/cm^2)	Capacity to 0.0V (A-hr)	Maximum Temp. (°C)	Maximum Pressure (psig)	Mid-discharge Voltage (V)
C-C-W-18	0.2	1.0	5.18	35	15	3.50
C-C-W-19	2.0	10.0	4.46	76	78	3.30
C-C-W-20	2.0	10.0	4.57	92	74	3.30
C-C-W-21*	3.0	15.0	3.90	143	210	3.20
C-C-W-22	3.0	15.0	3.96	147	216	3.20
C-C-W-23	3.0	15.0	4.05	149	228	3.20
C-C-W-24*	4.0	20.0	3.53	185	315	3.15
C-C-W-25*	4.0	20.0	3.67	185	293	3.10

*Cells vented.

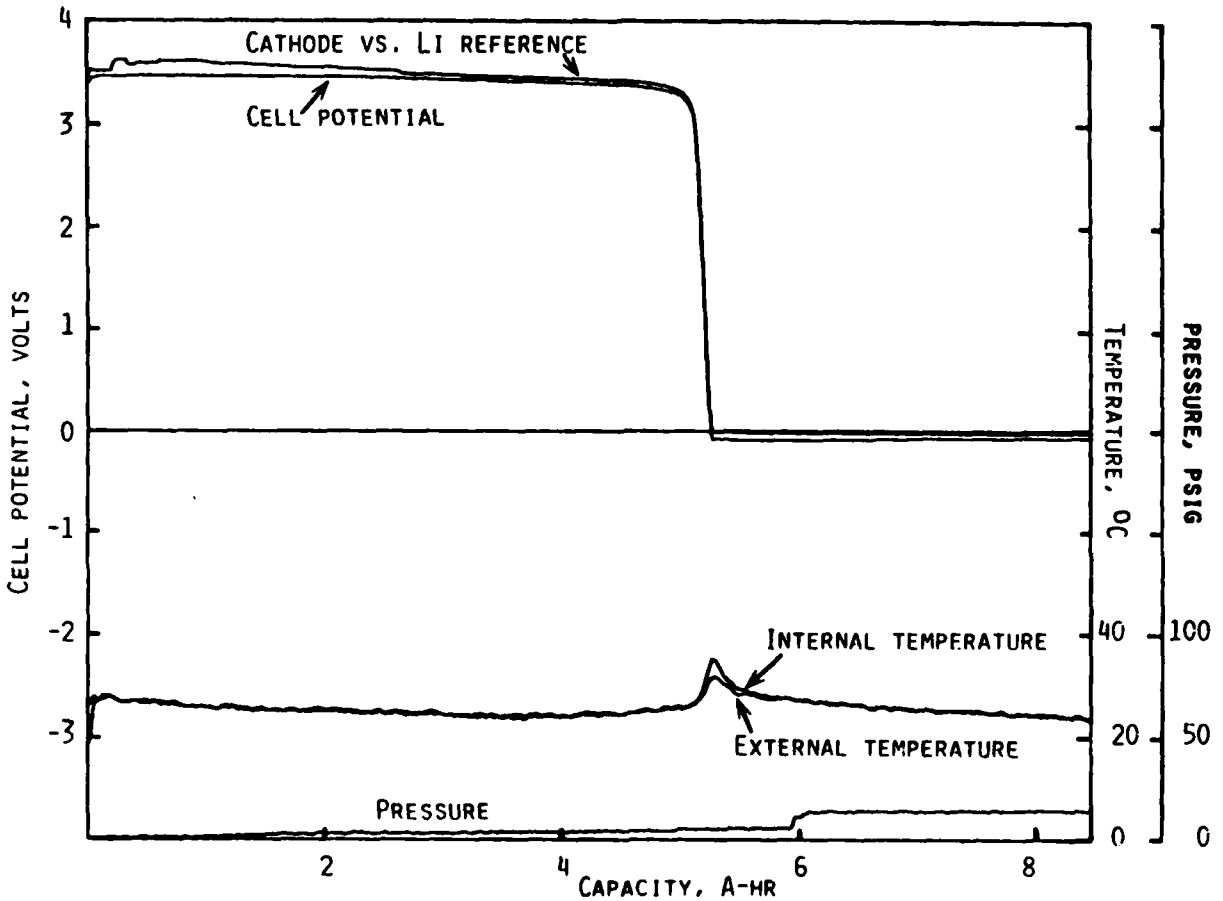


FIGURE 20. DISCHARGE DATA FOR CELL C-C-W-18 AT 0.2A AND 20°C

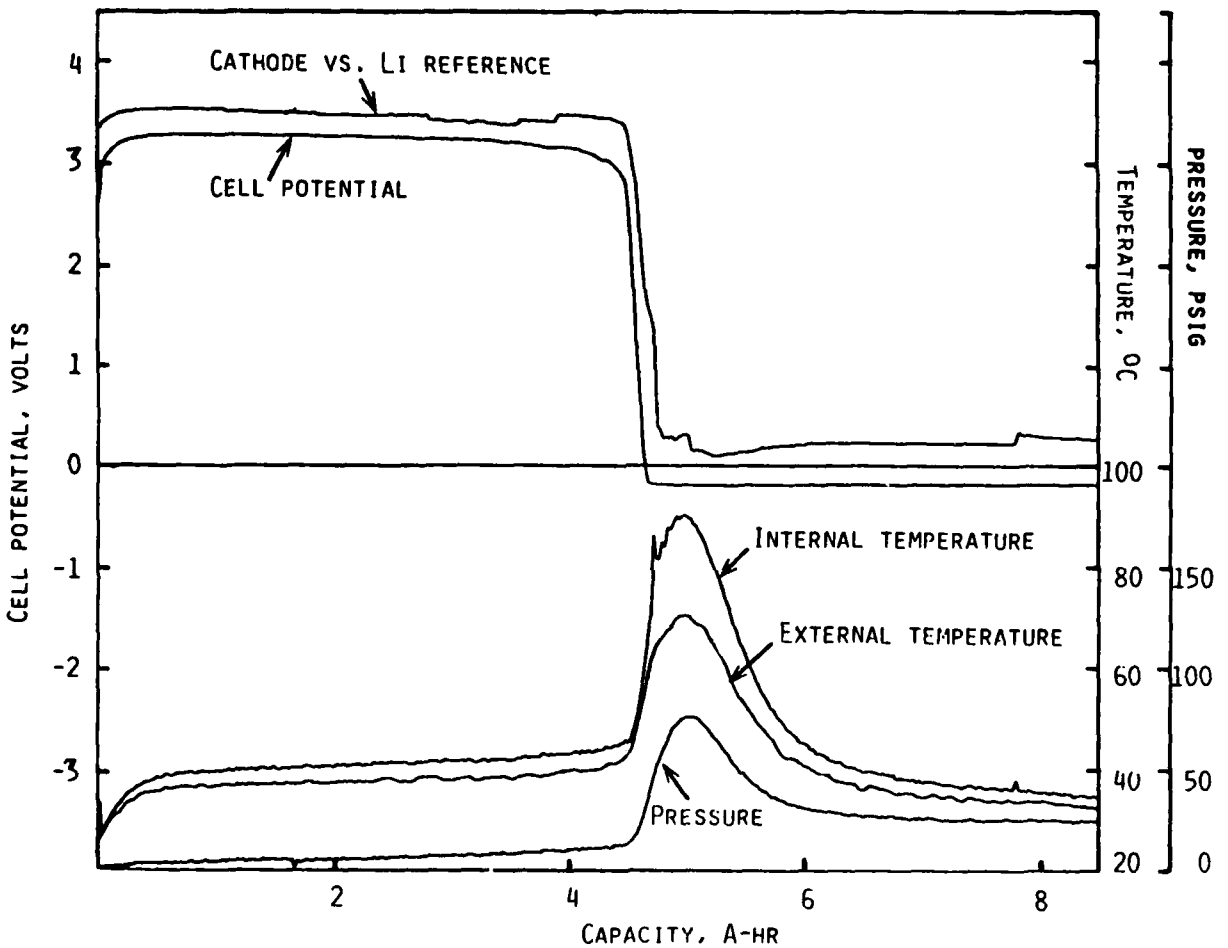


FIGURE 21. DISCHARGE DATA FOR CELL C-C-W-20 AT 2.0A AND 20°C

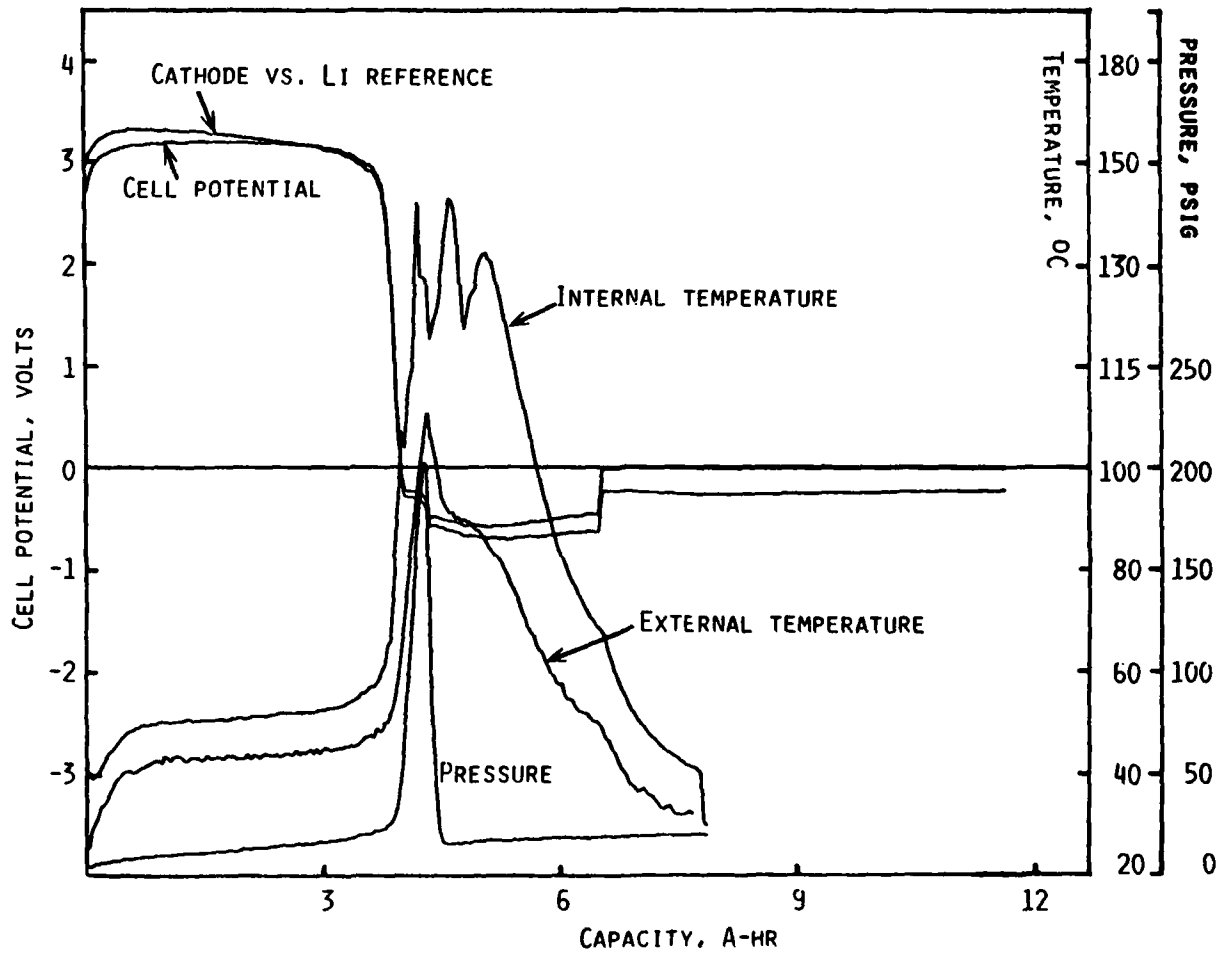


FIGURE 22. DISCHARGE DATA FOR CELL C-C-W-21 AT 3.0A AND 20°C

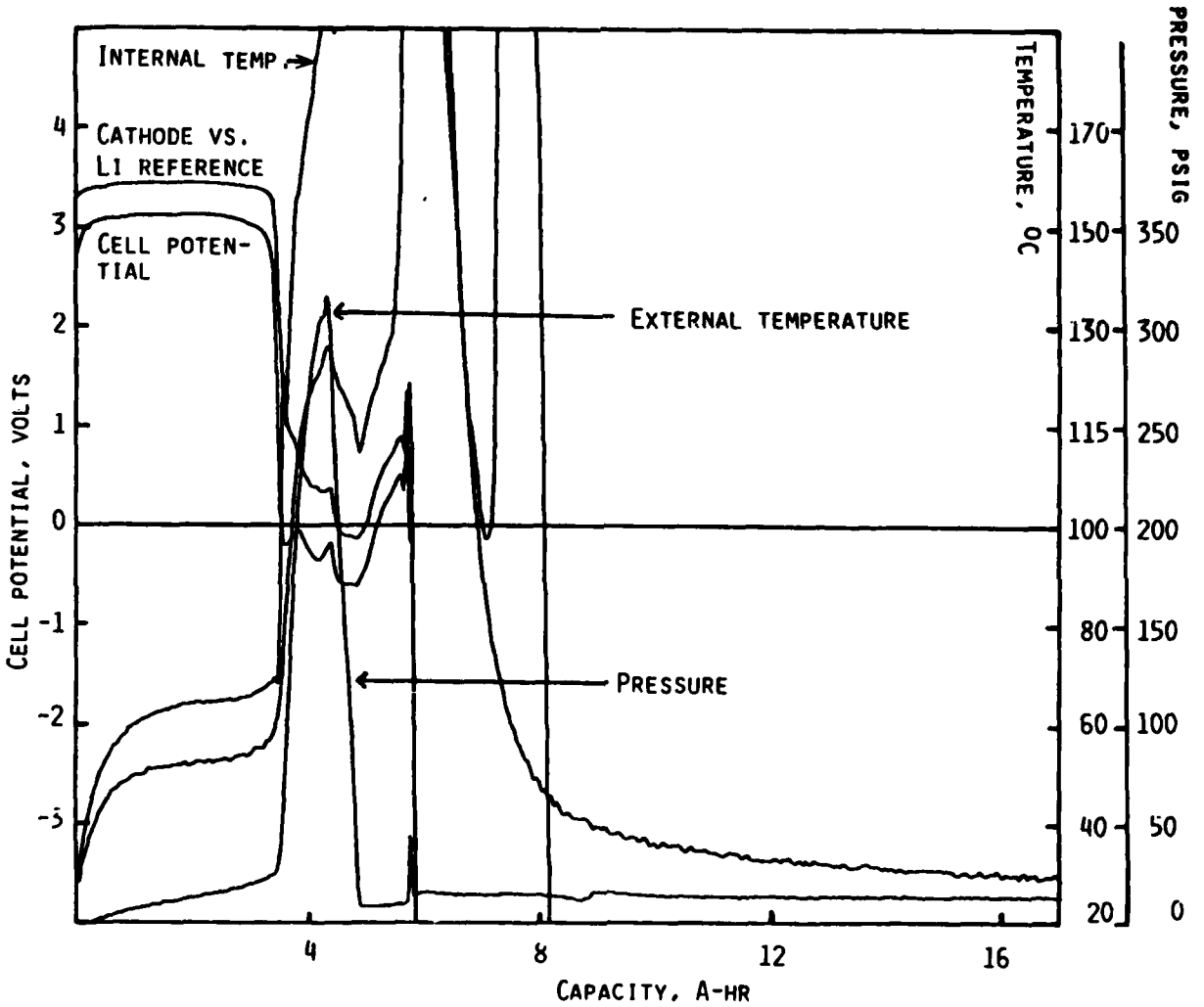


FIGURE 23. DISCHARGE DATA FOR CELL C-C-W-24 AT 4.0A AND 20°C

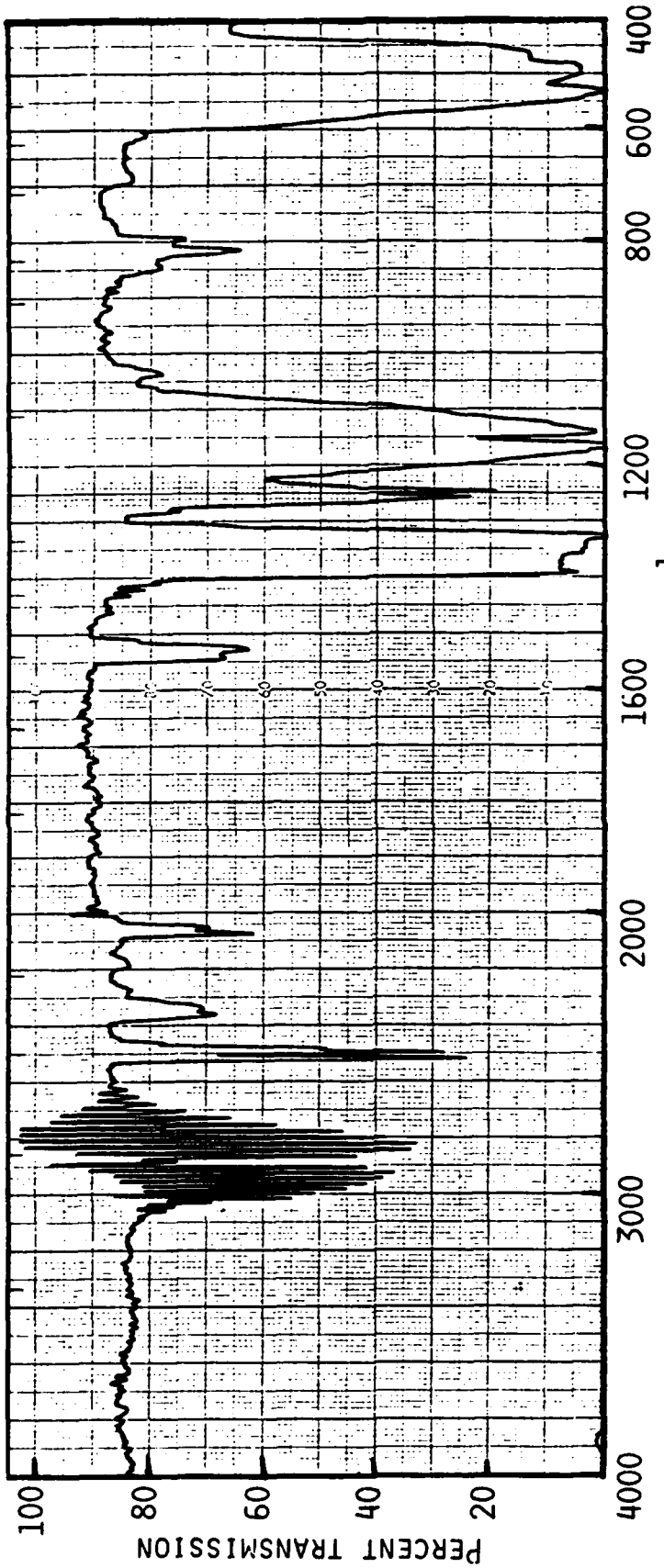


FIGURE 24. GAS IR SPECTRUM FROM CELL C-C-W-24

TABLE 8. PERFORMANCE OF CATALYZED CATHODE-LIMITED WET CELLS AT -12°C

Cell Number	Discharge Current (A)	Current Density (mA/cm^2)	Capacity to 0.0V (A-hr)	Maximum Temp. (°C)	Maximum Pressure (psig)	Mid-discharge Voltage (V)
C-C-W-26	0.2	1.0	4.68	0	0	3.27
C-C-W-27	2.0	10.0	3.78	70	-	2.95
C-C-W-28	2.0	10.0	3.96	66	15	2.95
C-C-W-29	3.0	15.0	3.62	84*	110	2.90
C-C-W-30	3.0	15.0	2.86	81*	96	2.72
C-C-W-31	3.0	15.0	2.41	122	110	2.87
C-C-W-32**	4.0	20.0	2.98	132	-	2.89
C-C-W-33**	4.0	20.0	2.48	>185	115	2.70

* External cell temperature.
**Cell vented.

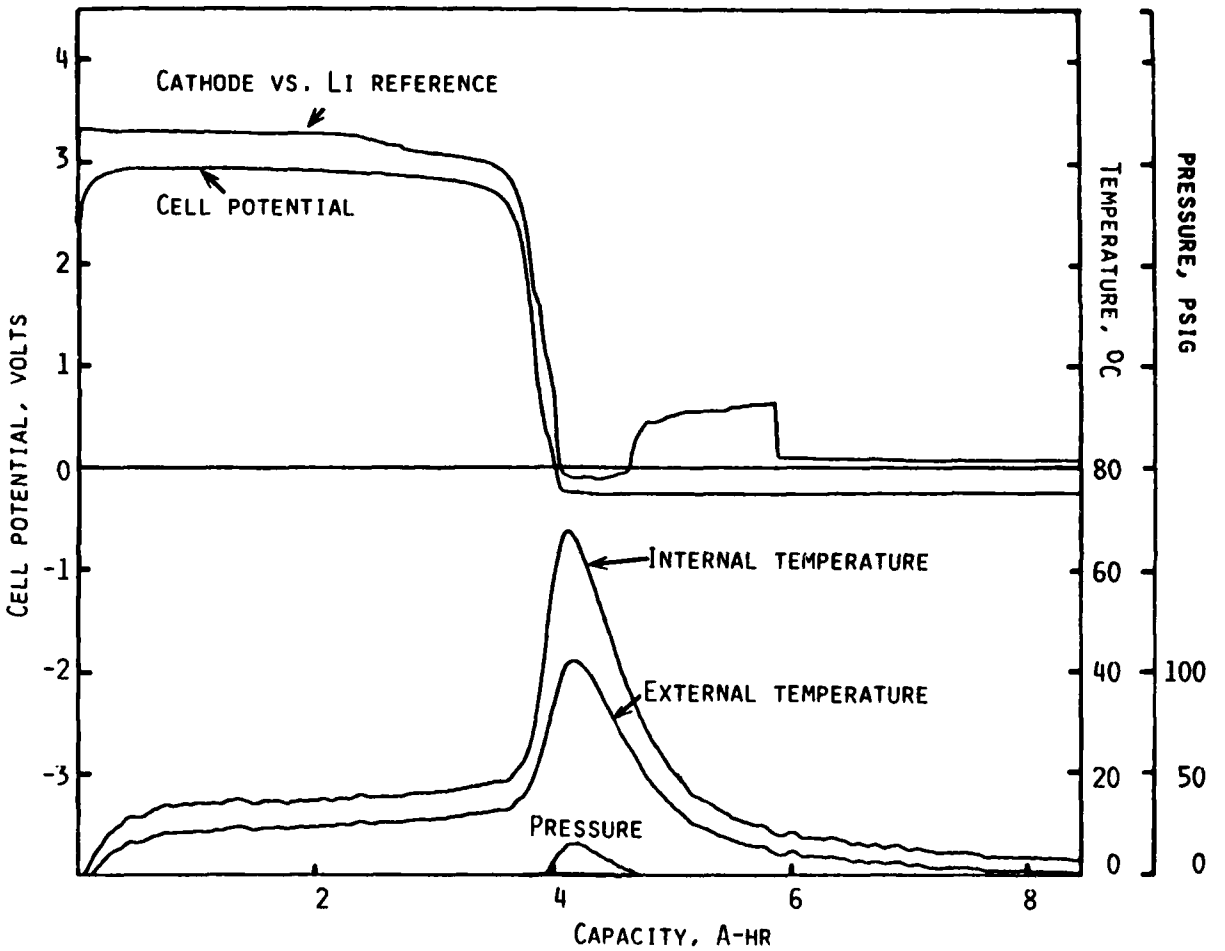


FIGURE 25. DISCHARGE DATA FOR CELL C-C-W-28 AT 2.0A AND –12°C

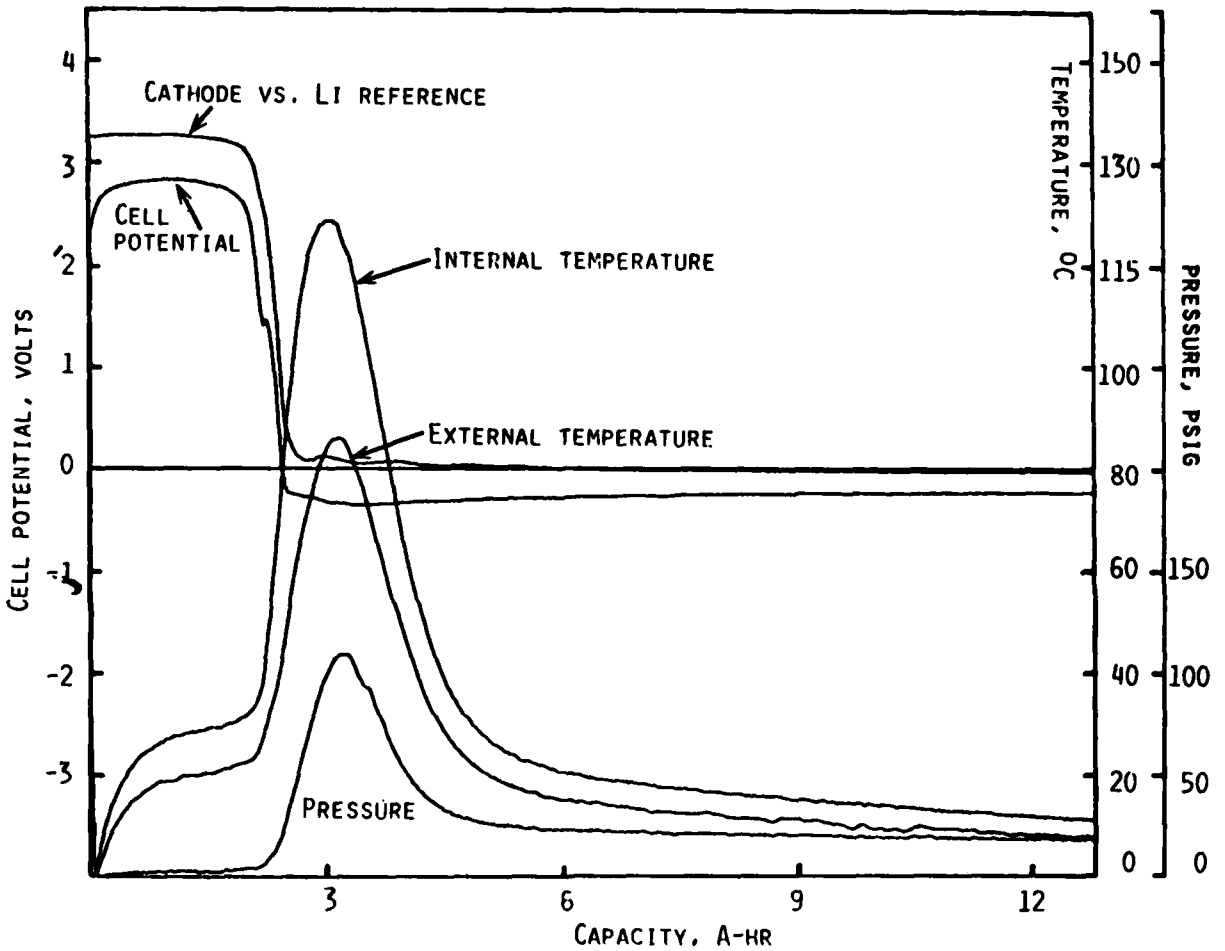


FIGURE 26. DISCHARGE DATA FOR CELL C-C-W-31 AT 3.0A AND −12°C

CHAPTER 4

DISCUSSION

Table 9 summarizes the effect of water on the average capacities of uncatalyzed and catalyzed cells discharged at a 2.0A rate. Although the averages were limited to a small number of cells, 56 in all, a clear pattern was established. The capacity of uncatalyzed cells, especially Li-limited, decreased when water was present. However, water caused little change in the capacity of the catalyzed cells. The overall effect was less apparent in cathode limited cells, where the capacity decreased ~4 percent in uncatalyzed cells and increased ~7 percent in catalyzed cells, a net change of approximately 11 percent. The most pronounced results occurred in Li-limited cells. One would not expect a cathode catalyst to have any noticeable effect on Li-limited cells where the cell capacity was limited by the amount of lithium. Indeed this was confirmed in the cells without water--the addition of a catalyst did not alter the capacity of Li-limited cells at either 20°C or -12°C. In Li-limited cells containing water, the catalyst had a dramatic effect on cell capacity. Consider the Li-limited cells at -12°C. With or without a catalyst the cell capacity in the dry cell is 2.90 Ahr. Water decreases this capacity ~18 percent in the uncatalyzed cell. A 9 percent increase was observed in the catalyzed cells--a net change of ~27 percent. The conclusion is that although a catalyst has little effect on cell capacity of "dry" Li-limited cells, the cell performance of Li-limited cells that contain moisture can be greatly enhanced by a catalyst. The data indicate this catalyst may serve a dual purpose in the $SOCl_2$ system by gettering water from the system, thus reducing parasitic corrosion processes at the lithium anode and enhancing the carbon cathodes capacity.

The actual percentage change in the average cell capacity due to addition of the (Co-TAA) catalyst is summarized for both wet and dry cells in Table 10. The most noticeable improvement occurs in: (a) wet Li-limited cells, (b) in carbon-limited cells discharged at high rates at 20°C--a 61.2 percent capacity increase occurs at 3.0A compared to a 20.3 percent increase at the lower 2.0A rate, and (c) dramatic increase in capacity of carbon-limited cells discharged at -12°C even at low rates.

The data indicate the catalyst is most effective on enhancing cell performance at high rates. Two examples can be cited. (a) Catalyzed Li-limited cells were discharged at 20°C at 2.0A and 4.0A rates. The cell capacities (averaged for both wet and dry cells) were identical (3.05 Ahr) for both discharge rates. (b) Table 9 shows the average capacity of uncatalyzed cathode limited cells at -12°C is 2.1 Ahr at the 2.0A rate. The same cells containing the catalyst discharged at -12°C but at double the rate, 4.0A, had an even larger average capacity of 2.73 Ahr.

TABLE 9. THE EFFECT OF WATER ON DISCHARGE CAPACITY OF CATALYZED AND UNCATALYZED Li/$SOCl_2$ CELLS

		AVERAGE CAPACITY (Ah) AT 2.0A RATE TO 0.0V			
		UNCATALYZED		CATALYZED	
TEMP. °C	CELL BALANCE*	DRY	WET	DRY	WET
20	A	2.95	2.63	2.98	3.15
-12	A	2.90	2.37	2.90	3.17
20	C	3.59	3.42	4.32	4.52
-12	C	2.16	2.10	3.52	3.87

*A - lithium-limited
C - carbon-limited

TABLE 10. EFFECT OF CATALYST ON INCREASING THE AVERAGE CELL CAPACITY

			INCREASING IN AVERAGE CELL CAPACITY, %	
TEMP. °C	DISCHARGE RATE, (A)	CELL* BALANCE	DRY	WET
20	2.0	A	1.0	19.8
20	2.0	C	20.3	32.2
20	3.0	C	61.2	--
-12	2.0	A	0	33.8
-12	2.0	C	63.0	84.3

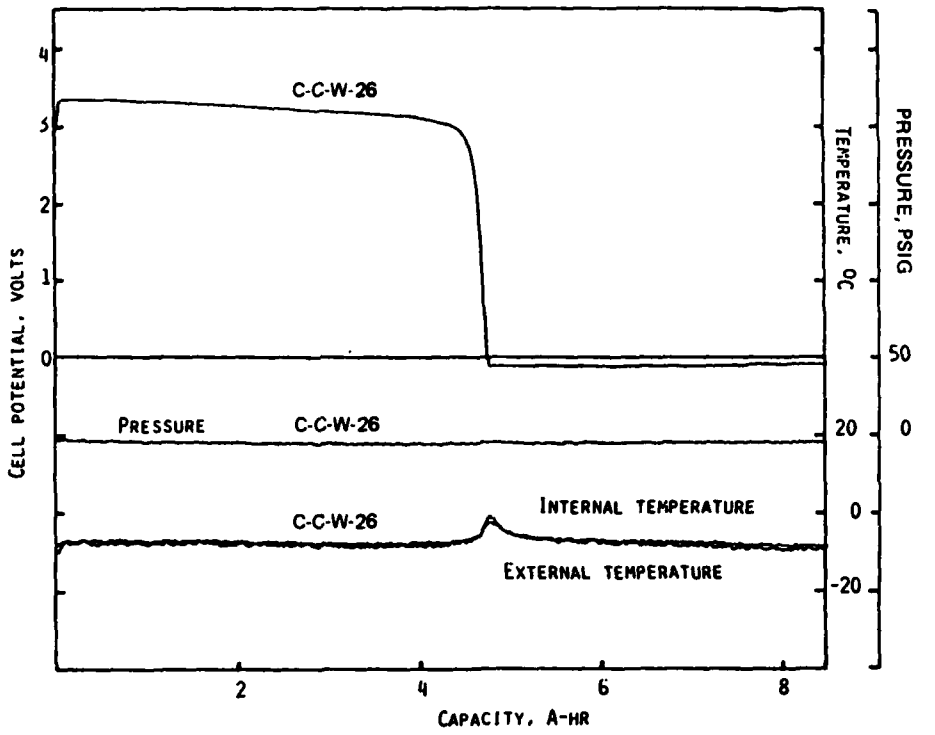
*A - lithium-limited
C - carbon-limited

The catalyst also improved the capacity of carbon-limited cells even at the low rates of 0.2A. Similar cells with and without catalyst discharged at 0.2A at -12°C are illustrated in Figure 27.

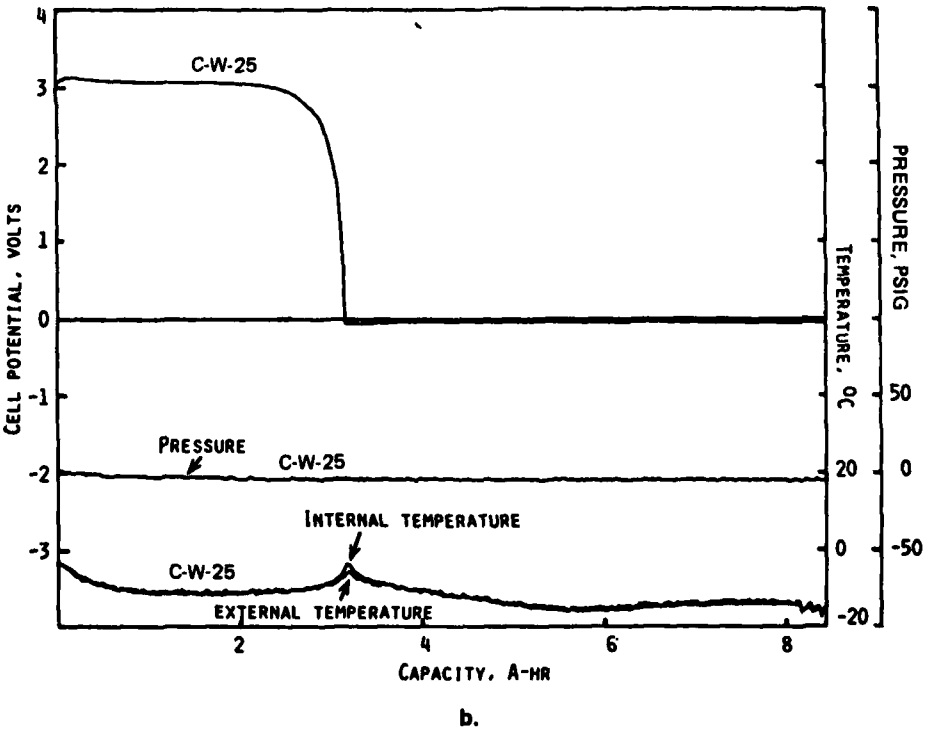
Table 11 summarizes the effect of water on cell hazards in catalyzed $SOCl_2$ cells discharged at the 4.0A rate. The data show that wet electrolyte cells generated more pressure and were more hazardous than dry cells. Of the 14 cells tested, 5 of the 6 dry cells did not vent and 7 of the 8 wet cells did vent. The wet cell that did not vent was the only Li-limited cell discharged at -12°C. The wet cathode limited cells discharge at 4.0A had higher internal temperatures. Although catalyzed Li-limited cells performed exceptionally, few of these cells were tested at high rates. The effect of catalyst on Li-limited cells was limited since uncatalyzed Li-limited cells became cathode limited when discharged at 3.0A or higher. Wet catalyzed cathode limited cells discharged at -12°C at the 3.0A rate exhibited large fluctuations in capacity. This may have arisen from an anodic polarization as cited in the first report. Since this behavior was not observed with the dry cells under similar conditions, water may be a factor in the anodic polarization process.

Generally, wet cells were also observed to develop greater pressures than dry cells during storage.

The data show that cathode limited cells always generated greater internal temperatures than anode limited cells. For example, the average maximum temperature of cathode limited cells discharged at 20°C at 2.0A was ~101°C compared to 66°C recorded in the anode limited cells. The amount of carboneous gases, such as CO_2 etc., was generally found in the greatest concentrations in (a) vented cells, (b) cathode limited cells, and (c) cells discharged at high rates. More specifically, cells which exhibited the largest temperature rises produced the most carboneous gases. Indeed the amount of COS generated was strongly dependent on cell temperature. The anode limited cell, C-A-W-21, discharged at 5.0A recorded high temperatures and significant amounts of COS gas. Carbon disulfide together with large amounts of CO_2, HCl, COS (Figure 24) was observed in cell C-C-W-24 which vented violently. However, as Table 11 shows, the cells that vented at high discharge rates generally contained water. These cells also displayed the greatest amounts of HCl gas. As illustrated by the IR spectra in Figure 16, no HCl was observed in a dry cathode limited cell discharged at 3.0A. Still there was a substantial amount of COS.



a.



b.

FIGURE 27a. & b. COMPARISON OF CATALYZED (C-C-W-26) AND UNCATALYZED (C-W-25) CATHODE – LIMITED WET CELLS DISCHARGED AT 0.2A AND –12°C

TABLE 11. SUMMARY OF THE EFFECT OF WATER ON HAZARDS IN CATALYZED $Li/SOCl_2$ CELLS DISCHARGED AT A 4.0A RATE

CATHODE LIMITED CELLS

CELL NO.	TEMP. °C	CONDITION	OBSERVATION
C-C-W-24	20	Wet	Vented
C-C-W-25	20	Wet	Vented
C-C-W-32	-12	Wet	Vented
C-C-W-33	-12	Wet	Vented
C-C-D-8	20	Dry	Vented
C-C-D-9	20	Dry	No Venting
C-C-D-16	-12	Dry	No Venting
C-C-D-17	-12	Dry	No Venting

LITHIUM-LIMITED CELLS

CELL NO.	TEMP. °C	CONDITION	OBSERVATION
C-A-W-21*	20	Wet	Vented
C-A-W-19	20	Wet	Vented
C-A-W-20	20	Wet	Vented
C-A-D-8	20	Dry	No Venting
C-A-D-9	20	Dry	No Venting
C-A-W-26	-12	Wet	No Venting

*Discharged at 5.0A rate

CHAPTER 5

CONCLUSIONS

Improved performance and safety was achieved in C-size Li/$SOCl_2$ cells using Co-TAA catalyst. The catalyst was most effective at high rates or low temperature operation. Cells discharged at -12°C had larger capacities at the 4.0A rate than uncatalyzed cells at the 2.0A rate. In general, the catalyst increased the cell capacity substantially while enhancing the operating voltage approximately 10 percent. The greatest improvement occurred in cathode-limited cells discharged at high rates at both 20° and -12°C and in wet Li-limited cells. The safety of cell operation was also enhanced by use of the catalyst. For instance, uncatalyzed Li-limited cells became cathode limited at the 3.0A rate Cathode limited cells are considered more hazardous than Li-limited cells. The use of Co-TAA enabled the lithium-limited cells to remain lithium-limited. The cell discharged at the 5.0A rate remained Li-limited. In addition, there was generally less internal heating in catalyzed cells, especially in the wet cells.

The amounts of COS detected in the gas phase appeared to be dependent on the internal temperature. The greatest concentration of COS was found in cells with highly elevated temperatures. HCl gas was most often found in wet cells with high internal temperatures.

The catalyst served to negate the capacity lowering effect of water. But, at high rates of discharge (4.0A) water increased the likelihood of cell venting.

Previous studies proposed an SO_2 free $SOCl_2$ discharge mechanism.[1,2] IR analyses of the gas phase of several cells revealed that SO_2 is a major product in catalyzed cells.

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